BALLONA CREEK METALS TMDL

AND

BALLONA CREEK ESTUARY TOXIC POLLUTANTS TMDL

COORDINATED MONITORING PLAN

PREPARED BY THE MONITORING PLAN SUBCOMMITTEE
CHAIRED BY CITY OF LOS ANGELES

Submitted
JANUARY 10, 2007

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APPENDICES

LIST OF ACRONYMS

µg/L	Microgram per Liter
APHA	American Public Health Association
AWWA	American Water Works Association
BC	Ballona Creek
BCE	Ballona Creek Estuary
BMPs	Best Management Practices
CADOHS	California Department of Health Services
Cal/OSHA	California Occupational Safety & Health Administration
Caltrans	California Department of Transportation
CCD	Charged Coupled Device
CDFG	California Department of Fish and Game
Cent	Centinela
cfs	Cubic Feet per Second
CHP	Chemical Hygiene Plan
CLABOS	City of Los Angeles Bureau of Sanitation
CMP	Coordinated Monitoring Plan
COC	Chain-of-Custody
COMM	Commercial and Sport Fishing
CTR	California Toxics Rule
CWA	Clean Water Act
DDT	Dichloro Diphenyl Trichloroethane
DMR	Discharge Monitoring Report
ELAP	Environmental Laboratory Accreditation Program
EMC	Even Mean Concentration
EMD	Environmental Monitoring Division
ERL	Effects Range Low
EST	Estuarine Habitat
FACT	Fast Automated Curve-fitting Technique
g/day	Gram per day
g/yr	Gram per Year
GIS	Geographic Information System
ICP	Inductively Coupled Plasma
ICSD	Information & Control System Division
kg/yr	Kilogram per Year
LADPW	Los Angeles County Department of Public Work
LARWQCP	Los Angeles Regional Water Quality Control Board
LIMS	Laboratory Information Management System
m^3/yr	Cubic Meter per Year
MAR	Marine Habitat
mg/kg	Milligram per Kilogram
mg/L	Milligram per Liter
MIGR	Migration of Aquatic Organisms
MPH	Mile per Hour
MS4	Municipal Separate Storm Sewer System

mt/m^3	Metric Ton per Cubic Meter
Nat	National
NIST	National Institute of Standards and Technology
NOAA	National Oceanic and Atmospheric Administrations
NPDES	National Pollutant Discharge Elimination System
NRDC	Natural Resources Defense Council
PAHs	Polynuclear Aromatic Hydrocarbons
PCBs	Polychlorinated Biphenyls
PE	Performance Evaluation
QA/QC	Quality Assurance/Quality Control
RARE	Rare and Threatened or Endangered Species
REC1	Water Contact Recreation
REC2	Non-contact Water Recreation
RF	Radio Frequency
RPD	Relative Percent Difference
RWQCB	Regional Water Quality Control Board
SHELL	Shellfish Harvesting
SOP	Standard Operating Procedure
SPWN	Reproduction and Early Development of Fish
TIE	Toxicity Identification Evaluation
TMDL	Total Maximum Daily Load
TOC	Total Organic Carbon
USEPA	United States Environmental Protection Agency
WARM	Warm Freshwater Habitat
WEF	Water Environmental Federation
WILD	Wildlife Habitat
WLAs	Waste Load Allocations
WP	Water Pollution
WPD	Watershed Protection Division

1.0 EXECUTIVE SUMMARY

The U.S. Federal Regulations under the Clean Water Act (CWA) of 1972 require States to develop a list of impaired waters and the pollutants for which they are impaired, also known as the 303 (d) List. Subsequently, States must establish a watershed-based pollutant specific Total Maximum Daily Load (TMDL) to bring impaired water bodies into compliance with the water quality standards necessary for its beneficial uses. This TMDL is then incorporated as an amendment to the regional Basin Plan. The designated responsible jurisdictions and responsible agencies must then reduce their discharges to meet these waste load allocations according to a compliance schedule.

Segments of Ballona Creek, Sepulveda Canyon Channel and Ballona Creek Estuary were designated as impaired and included on California's 1996, 1998, and 2002 CWA 303(d) lists of impaired waters due to excessive amounts of certain metals, organic compounds, and toxicity. The presence of these constituents in surface waters and sediments is an indication that water and sediment quality may not be sufficient to maintain the various beneficial uses specified in the Basin Plan for these water bodies. The California Regional Water Quality Control Board, Los Angeles Region (Regional Board) released a first draft of the Ballona Metals (Creek) and Ballona Creek Estuary (Estuary) Toxics TMDLs on March 28, 2005. The Creek Metals and Estuary Toxics TMDLs became effective on January 11, 2006, when they were approved by USEPA.

While the City of Los Angeles is the primary jurisdictional group for the Creek Metals and Estuary Toxics TMDLs, Cities of Los Angeles, Culver City, Beverly Hills, Inglewood, West Hollywood, Santa Monica, the County of Los Angeles, and Caltrans are jointly responsible for meeting the TMDL requirements. The Creek Metals and Estuary Toxics TMDLs require responsible agencies within the watershed to achieve compliance with the TMDL, according to specified schedules. Five years after January 11, 2006, the effective date of the Creek Metals TMDL and six years after January 11, 2006, the effective date of the Estuary Toxics TMDL, the Regional Board will re-open the TMDLs to re-evaluate the waste load allocations and the implementation schedules.

Introduction

This Coordinated Monitoring Plan was developed by the Monitoring Plan Subcommittee chaired by the City of Los Angeles, with the input from the Regional Board, Heal the Bay, and Santa Monica BayKeeper. The plan is designed to comply with the monitoring requirements of the Creek Metals and Estuary Toxics TMDLs and to provide the data to support the re-evaluations that will be made when the TMDLs are reopened in five and six years, respectively.

The Creek Metals TMDL establishes waste load allocations (WLAs) based on the California Toxics Rule (CTR) criteria. The Estuary Toxics TMDL establishes WLAs based on the National Oceanic and Atmospheric Administration (NOAA) Effects Ratio-Low (ER-L) sediment quality guidelines.

The Creek Metals and Estuary Toxics TMDLs require that one year after their effective date, responsible jurisdictions and responsible agencies must submit a Coordinated Monitoring Plan for these.

Historical or existing monitoring sites are those locations monitored by the City of Los Angeles Bureau of Sanitation, Environmental Monitoring Division (EMD), and the Los Angeles County Department of Public Works (LACDPW) at the time of adoption of this TMDL by the Regional Board.

Monitoring Sites

The monitoring program will begin as soon as it is practicable after the Coordinated Monitoring Plan is approved by the RWQCB. The proposed monitoring program for water quality, stormwater and storm-borne sediments consists of four Tier I sampling sites and six Tier II monitoring sites. Tier II sites represent portions of the total drainage area upstream of the Tier I sites. Tier II sites will not be sampled unless there are exceedances of the WLA(s) in their respective downstream Tier I sites. Water quality samples will be collected monthly. Storms will be sampled as they occur, provided that the time lag between storm evens is greater than 72 hours. In the case where the second storm event follows the first by less than 72 hours, it will not be sampled due to resource and logistical concerns. A pilot study will be established, prior to the start of effectiveness monitoring, to capture storm-borne sediment from stormwater samples. If it should prove to be impractical to collect sufficient amounts of sediments by this method, the Jurisdictional Group will propose an alternative method to the RWQCB. Six sediment quality monitoring locations are established. Sampling will be done semi-annually during the first year of monitoring and annually thereafter. Two bioaccumulation sites are established for sport fish and four bioaccumulation sites are established for collection of mussels. Bioaccumulation sampling will be performed annually.

Materials and Methods

Samples will be tested by a State of California Environmental Laboratory Accreditation Program (ELAP) certified laboratory using ELAP approved methods.

Quality assurance and quality control procedures will be conducted to confirm that the analytical data collected are valid and that they are comparable among all participating laboratories.

Data Management and Reporting

All monitoring agencies performing analyses for this program will submit their data electronically to the City of Los Angeles's Bureau of Sanitation on an annual basis. The final summary reports will be submitted to the Regional Board on an annual basis along with compliance summary tables. Copies of the annual reports will be distributed to the responsible agencies prior to submittal to the Regional Board.

2.0 INTRODUCTION

This monitoring proposal is submitted to fulfill the requirement for developing a Coordinated Monitoring Plan for the Ballona Creek (Creek) Metals and Ballona Creek Estuary (Estuary) Toxic Pollutants Total Maximum Daily Loads (TMDL). As reference, the TMDL basin plan amendments can be found in Appendices L, I, and J of this document or the entire TMDL documents, including the staff report, can be found on the Los Angeles Regional Water Quality Control Board's (Regional Board) website at http://www.swrcb.ca.gov/rwqcb4/.

2.1 Background

Federal Regulations under the Clean Water Act (CWA) require States to develop a list of impaired waters and pollutants for which they are impaired, also known as the 303(d) List. The States must then establish capacity of the water body to assimilate the impairing pollutants. This is done in the form of the pollutant TMDL that the water body can receive and still achieve the water quality objectives necessary to protect beneficial uses (e.g., REC1). Waste Load Allocations (WLA) from point sources and load allocations from non-point sources must be reduced as needed according to the schedule to meet the TMDL of the water body. These TMDLs are incorporated as amendments to the regional Water Quality Control Plan (Basin Plan).

Ballona Creek and Estuary were designated as impaired and included on California's 2002 and 1998 CWA §303(d) List of impaired waters, respectively. Segments of the Creek are listed for dissolved copper, lead, zinc, and total selenium. Segments of the Sepulveda Canyon Channel are listed for lead. The Estuary sediment is listed for cadmium, lead, silver, zinc, chlordane, DDT, PCBs, and PAHs. Discharges of toxic pollutants and metals to these water bodies may result in impairments of beneficial uses associated with aquatic life (WARM, EST, MAR, WILD, RARE, MIGR, and SPWN), and human use of these resources (COMM, SHELL, REC1, and REC2).

The Creek and Estuary Metals and Toxic Pollutants TMDLs were approved by the United States Environmental Protection Agency (EPA) and became effective on January 11, 2006 with the following actions required:

- The TMDLs require responsible jurisdictions and responsible agencies to submit a Coordinated Monitoring Plan within 12 months of the effective date of the TMDLs.
- Five years after the effective date of the Metals TMDL and six years after the effective date of the Toxics TMDL, the Regional Board will re-consider the TMDLs, including certain provisions based on new data, some of which will be collected under this monitoring plan.
- The Regional Board will reassess the TMDL's numeric targets and sediment WLAs consistency with the State Board six months after the State Sediment Quality Objectives are adopted.

- Responsible jurisdictions and responsible agencies are required to achieve conformance with the Metals TMDL according to specified schedules, delineated below.
    - Six years after the effective date of the TMDL, the MS4 and Caltrans storm water NPDES permittees shall demonstrate that 50% of the total drainage area served by the MS4 system is effectively meeting the dry-weather WLAs and 25% of the total drainage area served by the MS4 system is effectively meeting the wet-weather WLAs.
    - Eight years after the effective date of the TMDL, the MS4 and Caltrans storm water NPDES permittees shall demonstrate that 75% of the total drainage area served by the MS4 system is effectively meeting the dry-weather WLAs.
    - Ten years after the effective date of the TMDL, the MS4 and Caltrans storm water NPDES permittees shall demonstrate that 100% of the total drainage area served by the MS4 system is effectively meeting the dry-weather WLAs and 50% of the total drainage area served by the MS4 system is effectively meeting the wet-weather WLAs.
    - Fifteen years after the effective date of the TMDL, the MS4 and Caltrans storm water NPDES permittees shall demonstrate that 100% of the total drainage area served by the MS4 system is effectively meeting both the dry-weather and wet-weather WLAs.
- Responsible jurisdictions and responsible agencies are required to achieve conformance with the Estuary TMDL according to specified schedules, delineated below.
    - Seven years after the effective date of the TMDL, the MS4 and Caltrans storm water NPDES permittees shall demonstrate that 25% of the total drainage area served by the MS4 system is effectively meeting the WLAs for sediment.
    - Nine years after the effective date of the TMDL, the MS4 and Caltrans storm water NPDES permittees shall demonstrate that 50% of the total drainage area served by the MS4 system is effectively meeting the WLAs for sediment.
    - Eleven years after the effective date of the TMDL, the MS4 and Caltrans storm water NPDES permittees shall demonstrate that 75% of the total drainage area served by the MS4 system is effectively meeting the WLAs for sediment.
    - Fifteen years after the effective date of the TMDL The MS4 and Caltrans storm water NPDES permittees shall demonstrate that 100% of the total drainage area served by the MS4 system is effectively meeting the WLAs for sediment.

This monitoring proposal is submitted to fulfill the first of the above listed requirements, i.e., that the Coordinated Monitoring Plan for the Creek Metals and Estuary Toxic Pollutants TMDLs is to be submitted within 12 months of the effective date of the TMDL.

2.2 Waste Load Allocation Targets

The Coordinated Monitoring Plan must be designed to measure conformity with WLAs as defined in the TMDLs, and to provide some of the data to support the re-evaluations that will be made when the TMDLs are reconsidered in six years. In order to fully describe the Coordinated Monitoring Plan, a discussion of how the Regional Board will measure WLA conformity as stated in the TMDLs is necessary.

The Metals TMDL uses numeric water quality standards and conversion factors in the California Toxics Rule (CTR) to convert the numeric targets for dissolved copper, lead, and zinc to total recoverable copper, lead, and zinc. Since Ballona Creek is listed as impaired for total recoverable selenium, the CTR numeric targets were directly applied. Separate dry- and wet-weather standards are included because hardness values and flow conditions in the Creek vary between dry and wet-weather. The Estuary TMDL establishes numeric targets for cadmium, copper, lead, silver, zinc, chlordane, DDTs, Total PCBs, and Total PAHs, based on the National Oceanic and Atmospheric Administration's Effects Range-Low sediment quality guidelines. These numeric targets and the corresponding WLAs have been set based on the Los Angeles Basin Plan objectives for the various beneficial uses designated for Creek and Estuary along with the implementation provisions for these objectives.

As defined in the Metals TMDL, dry-weather is when the maximum daily flow in the Creek is less than 40 cubic feet per second (cfs), and wet-weather is when the maximum daily flow is equal to or greater than 40 cfs.

In the Estuary Toxics TMDL, conformance is based upon the levels of the above mentioned pollutants in storm-borne sediments. Additionally, the ambient monitoring portion of this TMDL requires dry-weather water quality, storm water, sediment quality, and bioaccumulation monitoring for the pollutants listed above.

A three-tiered approach will be employed to conform to the dry-weather, wet-weather, and storm-borne sediment effectiveness monitoring required by the Creek Metals and Estuary Toxics TMDLs. In Tier I, four sample points, each representing major portions of the total drainage area considering overlap, will be monitored. In Tier II, an additional six sample points, each representing between approximately 7 and 20% of the total drainage area, are identified. If data from one or more of the Tier I monitoring points exceeds any one of the criteria discussed in detail in section 3.3.1, the Tier II sample points, upstream of the affected Tier I sample point(s), will be placed in service for the analyses in question during the subsequent sample collection events.

If necessary, the Tier I and II testing results will be used to focus source-tracking efforts (Tier III) to elucidate and eliminate the source(s) of pollutants.

2.3 Coordinated Monitoring Plan Development

This monitoring plan was developed by the Ballona Creek Metals and Ballona Creek Estuary Toxics TMDLs Jurisdictional Group (Ballona Jurisdictional Group), which was chaired by the City of Los Angeles (see Appendix K for a list of participants).

The Ballona Jurisdictional Group began gathering information and meeting with representatives of the various agencies that had historically conducted monitoring within Ballona Creek, namely the City of Los Angeles Bureau of Sanitation and the Los Angeles County Department of Public Works. The group met on many occasions beginning in early 2005 to assess the plans for monitoring the TMDL requirements in the Creek and the Estuary and consists of representatives of the City of Los Angeles; the Los Angeles County Department of Public Works; the Cities of Beverly Hills; Culver City, Inglewood; Santa Monica; West Hollywood; and the California Department of Transportation.

2.4 Requirements of Coordinated Monitoring Plan

Both TMDLs require that within 12 months of the effective date:

> *"The MS4 and Caltrans storm water NPDES permittees must submit a coordinated monitoring plan, to be approved by the Executive Officer, which includes both ambient monitoring and TMDL effectiveness monitoring. Once the coordinated monitoring plan is approved by the Executive Officer ambient monitoring shall commence."*

The Metals TMDL requires the following:

> *"An ambient monitoring program is necessary to assess water quality throughout Ballona Creek and its tributaries and the progress being made to remove the metals impairments. The MS4 and Caltrans storm water NPDES permittees are jointly responsible for implementing the ambient monitoring program. The responsible agencies shall analyze samples for total recoverable metals and dissolved metals, including cadmium and silver, and hardness once a month at each monitoring location. The reported detection limits shall be lower than the hardness adjusted CTR criteria to determine if water quality objectives are being met."*

Furthermore, the Estuary Toxics TMDL requires the following:

> *"An ambient monitoring program is necessary to assess water quality throughout Ballona Creek and its tributaries and to assess the progress being made to remove the toxic pollutant impairments in Ballona Creek Estuary sediments. Data on background water quality for organics and sediments will help refine the numeric targets and WLAs and assist in the effective placement of BMPs. In addition, fish*

tissue data is required in Ballona Creek and Estuary to confirm fish tissue listings.

Water quality samples shall be collected monthly and analyzed for cadmium, copper, lead, silver, zinc, chlordane, dieldrin, DDT, total PCBs and total PAHs at detection limits that are at or below the minimum levels until the TMDL is reconsidered in the sixth year. The minimum levels are those published by the State Water Resources Control Board in Appendix 4 of the Policy for the Implementation of Toxic Standards for Inland Surface Water, Enclosed Bays, and Estuaries of California, March 2, 2000. Special emphasis should be placed on achieving detection limits that will allow evaluation relative to the CTR standards. If these cannot be achieved with conventional techniques, then a special study should be proposed to evaluate concentrations of organics.

The water quality samples collected during wet-weather, as part of the MS4 storm water monitoring program shall also be analyzed for total dissolved solids, settable solids and total suspended solids if not already part of the existing sampling program. Sampling shall be designed to collect sufficient volumes of settable and suspended solids to allow for analysis of cadmium, copper, lead, silver, zinc, chlordane, dieldrin, total DDT, total PCBx, total PAHs, and total organic carbon in the bulk sediment."

See Appendices I and J for more details on the TMDL requirements for the monitoring plan.

3.0 MONITORING SITES

3.1 Ballona Creek Watershed Setting

Ballona Creek Watershed is contained within the jurisdictions of eight responsible agencies: City of Los Angeles (lead), City of Beverly Hills, City of Culver City, City of Inglewood, City of West Hollywood, City of Santa Monica, County of Los Angeles, and Caltrans. The watershed is the largest subwatershed within the Santa Monica Bay Watershed Management Area, and is comprised of the West Los Angeles, Westwood Village, Culver City, Hollywood, Cienega, and Windsow Hills subwatersheds as defined by the Regional Board.

The combined size of the six subwatersheds is approximately 82,881 acres[1]; however, 13 acres of National Park Service and 414 acres of miscellaneous State and Federal lands are currently excluded. The RWQCB recommended that these areas be excluded at this time since they will be covered by separate NDPES permits issued by the Regional Board. This leaves 82,454 acres as the effective watershed area[2]. The effective watershed area falls under the jurisdiction of the following responsible agencies:

City of Los Angeles (lead)	67,053	acres
County of Los Angeles	3,928	acres
City of Beverly Hills	3,630	acres
City of Culver City	3,234	acres
City of Inglewood	1,934	acres
City of West Hollywood	1,201	acres
City of Santa Monica	265	acres
Caltrans	1,206	acres

Ballona Creek flows as an open channel for just under 10 miles from Los Angeles (South of Hancock Park) through Culver City, reaching the Santa Monica Bay just south of Marina del Rey. The transition between the Creek and Estuary is considered to occur at Centinela Boulevard; Ballona Creek above Centinela Boulevard is concrete-lined and Ballona Creek below Centinela Boulevard is soft bottom.

Several monitoring efforts have taken place within the Ballona Creek watershed. Beginning in 2002, the City of Los Angeles, Department of Public Works, Bureau of Sanitation, Watershed Protection Division, under its Status and Trends Monitoring Program, began monitoring at three (3) locations along the main channel of Ballona Creek for bacteria, metals, and other pollutants. In 2005 the Status and Trends Program was extended to include four (4) tributary monitoring locations. In addition, the County of Los Angeles, as part of the Los Angeles County Municipal Stormwater Permit, under its Core Monitoring

[1] Area breakdown was generated in GIS using Regional Board Data

[2] The overall effective watershed area may change depending on how the Regional Board decides to enforce National Parks Service and miscellaneous State and Federal areas to comply with the TMDLs.

Program, conducts sampling within the Ballona Creek watershed. The County's Core Monitoring Program is comprised of one permanent mass emission station (S01) within the main channel, six tributary locations, five estuary locations, and one bioassessment location. During the 2004-2005 wet-weather season, the six mass emission sites located on tributaries to the main channel of Ballona Creek were monitored. Five storm events and two dry-weather events were monitored at each tributary mass-emission station.

The monitoring sites for the Metals and Toxics TMDL have been selected by the Jurisdictional Group with guidance from the Monitoring Subcommittee. Guidance from the subcommittee took the form of a set of site selection guidelines listed below. These site selection guidelines were intended as overarching parameters for use by the responsible agencies to establish locations. Final selection of sampling locations required the exercise of professional judgment at the stakeholder level.

3.2 Site Selection Guidelines

These guidelines were used by the responsible agencies in establishing their Coordinated Monitoring Plan sites for effectiveness monitoring and ambient monitoring of the Ballona Creek Metals and Ballona Creek Estuary Toxics TMDLs. Each guideline was not necessarily relevant or applicable at every monitoring location.

Ballona Creek Metals and Estuary Toxics TMDLs

Dry- and Wet-Weather Water Quality and Storm-Borne Sediment Quality

1. Tier I - Sample points located in the 303(d) listed impaired water bodies, covering large portions of the total discharge area.
2. Tier II - Sampling locations will be reflective of the tributary areas, approximately 7 – 20% of the entire watershed area, upstream of Tier I locations.

Ballona Creek Estuary Toxics TMDL

Sediment Quality

1. A mixture of intentionally selected and randomly located sample points will be used.
2. Intentionally selected sample points will be located at a historical monitoring location and a highly utilized location to assess temporal data trends.
3. Randomly selected sample points will be used to
    a. Assess spatial distribution of target analyses within the estuary;
    b. Identify the area(s) of the estuary where the highest concentrations are located;

c. Determine whether the contaminants decrease farther from the source/sources;

Bioaccumulation

1. A mixture of intentionally selected and randomly located sample points will be used.
2. Intentionally selected sample points will be located at historical monitoring locations to assess temporal data trends.
3. Random sample points will be used to assess spatial bioaccumulation trends within the estuary.
4. If possible, sport fish species that are subject to human consumption will be targeted.
5. Should station location prohibit taking of sport fish, then any practical alternative fish species present will be used.

The Jurisdictional Group conducted a storm drain survey and consulted with as-built drawings and drainage maps to determine potential monitoring locations as part of the evaluation process. The final list of monitoring sites was selected based on requirements of the TMDLs and guidelines presented here; these sites are described in Section 3.3 of this plan and summarized in Appendix B.

3.3 Monitoring Locations

3.3.1 Wet- and Dry-Weather Water Quality and Storm-Borne Sediment Effectiveness Monitoring

Monitoring to comply with the Ballona Creek Metals TMDL establishes dry- and wet-weather water quality monitoring locations within the Ballona Creek watershed for two distinct purposes: to measure attainment of WLAs specified in the effectiveness monitoring portion of the TMDL and to characterize ambient water quality. Effectiveness monitoring utilizes the same dry- and wet-weather water quality monitoring locations within the Ballona Creek watershed as are used to characterize ambient water quality. Storm-borne sediment, captured at these monitoring locations, will be used to assess the status of meeting the WLAs established by the effectiveness monitoring program in the Estuary Toxics TMDL.

Water quality effectiveness monitoring will be accomplished through a three-tiered approach that will meet the TMDL requirements. Storm-borne sediment effectiveness monitoring will be performed at Tier I and Tier II sampling locations, as necessary. This monitoring approach will provide the responsible agencies with a predetermined set of locations to investigate sources of any possible exceedences that may occur at the conformance locations. Approximate locations of these sites are shown in the figure below. The associated drainage areas for these locations are outlined in Appendix B.

Tier I and II Monitoring Locations

The four Tier I sampling locations, each representing major portions of the total drainage area, are those locations, which have been identified as ambient monitoring locations in the Ballona Creek Metals TMDL and will also be used for effectiveness monitoring. Once effectiveness monitoring is required by the TMDL, the Tier II Activation and Deactivation Criteria listed below will be applied to the data from the Tier I locations to determine when monitoring at the upstream Tier II locations would begin and end in order to narrow the search for the source of the exceedances(s). Tier II locations were developed by further subdividing the watershed into smaller tributary areas that represent approximately 7% to 20% of the entire watershed.

Tier II Activation Criteria:

- There are 3 consecutive exceedances of the WLA(s) at a Tier I monitoring site.

Tier II Deactivation Criteria:

- Data from 3 consecutive Tier II monitoring events is less than the WLA(s).

Tier II monitoring will only be conducted at the Tier II sites that are directly upstream of the Tier I site where the WLA exceedances occurred. Tier II and Tier III monitoring will target only the constituent(s) that exceeded the WLA at the Tier I site. If it is found that a Tier II location is consistently not meeting the water quality standards, then Tier III monitoring will initiate a source tracking investigation to identify the source(s) causing the exceedances so that the responsible agencies can take the necessary corrective measures to resolve the problem. Auto samplers will be only installed at Tier II locations as indicated by the results from Tier I monitoring (i.e., there may be some Tier II locations installation of autosampler is not needed). Some Tier II Stations may require infrastructure design and construction before composite samplers can be installed. In these cases, if safety considerations allow grab sampling will be conducted during wet weather until auto-samplers are operational.

Tier I Locations

In accordance with the TMDL requirements, the responsible agencies propose to conduct monthly ambient/effectiveness sampling at Tier I locations. A brief description of the four Tier I locations (BC-1 through BC-4) in the 303(d) listed waterbodies, namely Reach 1, Reach 2, and Sepulveda (Canyon) Channel is given below. More details, including drainage maps and locations, of these sites are available in Appendix B.

<table>
<tr><td>Site Id: BC – 1*</td><td>Status: Existing</td><td>Location: Main Channel</td></tr>
<tr><td>Historical Site Id: Cent</td><td>Subwatershed: N/A</td><td></td></tr>
<tr><td colspan="2">Comments:
This is an existing sampling site currently monitored by the City of Los Angeles as part of its Status and Trends Monitoring Program. The site is located at Centinela Avenue on the main channel. This location receives flow from 88.8% of the total drainage area.</td><td>  </td></tr>
</table>

*Prior to the start of conformance monitoring, this location will be re-evaluated by the monitoring committee. Depending on the results from ambient monitoring, there may be no additional benefit to monitoring this location since there are no additional contributions downstream of BC-2.

Site Id: BC – 2	**Status:** Existing	**Location:** Main Channel
Historical Site Id: S01	**Subwatershed:** N/A	
Comments: This is the County of Los Angeles's existing mass emission monitoring site, which is located at the existing stream gage station (Stream Gage No. F38C-R) between Sawtelle Boulevard and Sepulveda Boulevard in the City of Los Angeles. This location, which was chosen to avoid tidal influences, receives flow from 70.0% of the total drainage area.		

Site Id: BC – 3	**Status:** Existing	**Location:** Main Channel
Historical Site Id: Nat	**Subwatershed:** N/A	
Comments: This is an existing sampling site currently monitored by the City of Los Angeles as part of its Status and Trends Monitoring Program. The site is located at National Boulevard on the main channel. This location receives flow from 37.5% of the total drainage area.		

Site Id: BC – 4	**Status:** Existing	**Location:** Tributary
Historical Site Id: TS08	**Subwatershed:** West Los Angeles	
Comments: This is an existing sampling site, located just above the confluence of Ballona Creek and the Sepulveda Channel. The location is currently monitored by the City of Los Angeles as part of its Status and Trends Monitoring Program, and was part of Los Angeles County's Core Monitoring Program under the LA County Municipal Stormwater Permit. This location receives flow from 18.1% of the total drainage area.		

Tier II Locations

Tier II monitoring locations consists of a total of six (6) sites where additional samples can be taken if data from Tier I locations are found to consistently exceed the effectiveness program WLAs. Several of these Tier II locations were used in LA County's Core Monitoring Program under the LA County Municipal Stormwater Permit. A description of each location follows:

Approximate locations of these sites are shown in Table 2 in Appendix B.

Site Id: BC – 5	**Status:** Existing	**Waterbody:** Tributary
Historical Site Id: TS09	**Subwatershed:** Benedict Canyon	
Comments: This is an existing sampling site, located just above the confluence of Ballona Creek and Benedict Canyon. The location is currently monitored by the City of Los Angeles as part of its Status and Trends Monitoring Program and was part Los Angeles County's Core Monitoring Program under LA County Municipal Stormwater Permit. This location receives flow from 9.1% of the total drainage area.		

Site Id: BC – 6	**Status:** New	**Waterbody:** Tributary
Historical Site Id: N/A	**Subwatershed:** Hollywood	
Comments: This is a new sample site near La Cienega within the storm drain prior to flow entering the main channel. This location receives flow from 7.1% of the total drainage area.		

Site Id: BC – 7	**Status:** Existing	**Waterbody:** Tributary
Historical Site Id: TS11	**Subwatershed:** Hollywood	
Comments: This is an existing sampling site, located near Fairfax Avenue that will be sampled within the storm drain prior to flow entering the main channel. The location is currently monitored by Los Angeles County's Core Monitoring Program under the LA County Municipal Stormwater Permit. This location receives flow from 8.0% of the total drainage area.		

Site Id: BC – 8	**Status:** Existing	**Waterbody:** Tributary
Historical Site Id: TS12	**Subwatershed:** Hollywood	
Comments: This is an existing sampling site, located near Cochran Avenue, which is the beginning of where Ballona Creek daylights. Sampling will be done within the storm drain prior to flow entering the main channel. The location was previously monitored by Los Angeles County's Core Monitoring Program under the LA County Municipal Stormwater Permit. This location receives flow from 19.8% of the total drainage area.		

Site Id: BC – 9	**Status:** Existing	**Waterbody:** Tributary
Historical Site Id: TS10	**Subwatershed:** Cienega	
Comments: This is an existing sampling site, located near Adams Boulevard that will be sampled within the storm drain prior to flow entering the main channel. The location was previously monitored by Los Angeles County's Core Monitoring Program under the LA County Municipal Stormwater Permit. This location receives flow from 1.7% of the total drainage area.		

Site Id: BC – 10	**Status:** New	**Waterbody:** Tributary
Historical Site Id: N/A	**Subwatershed:** Cienega	
Comments: This is a new sampling site, located near Jefferson Boulevard that will be sampled within the storm drain prior to flow entering the main channel. This location receives flow from 15.7% of the total drainage area.		

3.3.2 Ballona Creek Estuary Toxics TMDL

The Toxics TMDL ambient monitoring program requires dry-weather water quality, wet-weather water quality, estuary sediment, and bioaccumulation monitoring. Sediment-borne pollutant loading from the total drainage area into the Estuary during wet-weather is specified by the effectiveness monitoring program to measure conformance with the Ballona Creek Estuary Toxic Pollutants TMDL.

In accordance with the TMDL requirements, the responsible agencies propose to conduct dry-weather, wet-weather, and storm-borne sediment sampling from the same sample points and utilizing the same tiered scheme that is proposed for the Metals TMDL.

Sediment Quality

Six (6) sediment quality monitoring locations have been selected to meet the TMDL requirements as shown in the figure below. The TMDL states the stations will be randomly selected; however, as outlined below, the decision was made to propose 4 random locations and 2 intentionally selected historical locations to spatially cover the entire estuary. Additionally, these locations were evaluated and chosen based on special consideration to site accessibility, safety concerns, and sediment availability. Good faith efforts will be made to collect representative samples from each of the six locations. If samples cannot be obtained from the exact sample point, a reasonable attempt will be made to collect a sample from the vicinity of the sample point. If this proves unsuccessful, no sample will be collected from the given sample point. If samples cannot be collected during two consecutive sampling events, alternate sampling point(s) will be proposed to the RWQCB.

Approximate locations of these sites are shown in Table 3 in Appendix B.

Site Id: BCE – 1	**Status:** Existing	**Waterbody:** Estuary
Historical Site Id: BPTCP 44014.0	**Subwatershed:** N/A	
Comments: This is a historical station located at the mouth of Ballona Creek, which has existing data that can be used to determine temporal trends in pollutant concentrations.		

Site Id: BCE – 2	**Status:** Existing	**Waterbody:** Estuary
Historical Site Id: N/A	**Subwatershed:** N/A	
Comments: This is a fixed selected sampling site, located at the Pacific Street Bridge. This site has a high level of human contact, swimming, fishing (taking of fish, crabs, and mussels), kayaking, etc.		

Site Id: BCE – 3	**Status:** New	**Waterbody:** Estuary
Historical Site Id: N/A	**Subwatershed:** N/A	
Comments: This is a randomly selected sampling site, located between the Pacific Street Bridge and the self-regulating tide gate.		

Site Id: BCE – 4	**Status:** New	**Waterbody:** Estuary
Historical Site Id: N/A	**Subwatershed:** N/A	
Comments: This is a randomly selected sampling site, located between the Ballona wetlands tide-gate and Culver Blvd.		

Site Id: BCE – 5	**Status:** New	**Waterbody:** Estuary
Historical Site Id: N/A	**Subwatershed:** N/A	
Comments: This is a randomly selected sampling site, located between the Centinella Creek and Culver Blvd. Please note: the feasibility of collecting samples at this site is still being investigated.		

Site Id: BCE – 6	**Status:** New	**Waterbody:** Estuary
Historical Site Id: N/A	**Subwatershed:** N/A	
Comments: This is a randomly chosen station, located between the confluence with Centinela Creek and the upper boundary of the Ballona Creek Please note: the feasibility of collecting samples at this site is still being investigated.		

Bioaccumulation

To meet the TMDL requirements, the responsible agencies have selected two bioaccumulation monitoring locations to collect sport fish and four to collect mussels. The TMDL states the stations will be randomly selected; however, the responsible agencies propose to randomly select one fish and two mussel locations. One non-randomly selected site for collecting mussels is near BCE-1. The second non-randomly selected site for collecting mussels and the non-randomly selected site for collecting fish is BCE-2. The randomly selected sites for collecting mussels will be located near BCE-3 and BCE-4. BCE-4 is the randomly selected site for fish collection. Reasonable attempts will be made to collect two to three species of sport fish; but, if sport fish cannot be obtained, whatever species of fish that can be obtained will be used. Additionally, these locations were evaluated and chosen based on special consideration to site accessibility, safety concerns, and a high presence of fishing.

Descriptions of these sites can be found in the sediment section above. Approximate locations of these sites are shown in Table 4 in Appendix B.

3.4 TMDL Waste Load Allocations

The Creek dry-weather and wet-weather numeric water quality targets are based on chronic and acute CTR criteria, respectively. Copper, lead, and zinc targets are dependent on hardness. Since the WLAs for these metals are expressed as dissolved metals, the CTR factors were used to convert from dissolved to total recoverable metals. Hardness's of 77 mg/L and 300 mg/L as $CaCO_3$ were used to calculate the wet-and dry-weather default values listed in the TMDL. For these three metals, the exact conformance target is dependent upon the exact hardness of the sample. The CTR criteria for selenium are independent of hardness and are expressed as total recoverable rather than dissolved form of the metal. The dry-weather numeric targets and loading capacity and dry- and wet-weather WLAs are tabulated the RWQCB Basin Plan Amendment, located in Appendix I.

3.4.1 Storm-Borne Sediment Effectiveness Monitoring (Estuary Toxics TMDL)

Numeric targets for Ballona Creek Sediments are based on sediment quality guidelines compiled by the National Oceanic and Atmospheric Administrations (NOAA) Effects Range-Low (ER-L) guidelines, which are tabulated below in Table 3.1.

Table 3.1 NOAA ER-Ls

Constituent	ERL (mg/kg)
Cadmium	1.2
Copper	34
Lead	46.7
Silver	1.0
Zinc	150
Chlordane	0.5
DDTs	1.58
Total PCBs	22.7
Total PAHs	4022

Per the Estuary Toxics TMDL, "The loading capacity for Ballona Creek Estuary is calculated by multiplying the numeric targets by the average annual deposition of fine sediment, defined as silts (grain size 0.0625 millimeters) and smaller, within the Estuary by the bulk density of the sediment. The average annual fine sediment deposited is 5,004 cubic meters per year (m^3/yr) and the bulk density is 1.42 metric tons per cubic meter (mt/m^3). The TMDL is set equal to the loading capacity." The loading capacity for metals and organics is tabulated in the RWQCB Basin Plan Amendment, located in Appendix J.

4.0 MATERIALS AND METHODS

4.1 Sampling Schedule

The sampling schedule, for the various monitoring programs covered by this CMP, is tabulated below in Tables 4.1 – 4.5.

Table 4.1 Dry-Weather Water Quality

TMDL	Target Analyses	Monitoring Frequency
BC Metals	Copper Lead Selenium Zinc Hardness	Monthly
BC Estuary Toxics	Cadmium Copper Lead Silver Zinc DDTs Chlordane Dieldrin Total PCBs Total PAHs	Monthly

Table 4.2 Wet-Weather Water Quality

TMDL	Target Analyses	Monitoring Frequency
BC Metals	Copper Lead Selenium Zinc Hardness	One flow proportional composite sample over duration of selected wet-weather events. Please see Section 4.2 for further details.
BC Estuary Toxics	Cadmium Copper Lead Silver Zinc DDTs Chlordane Dieldrin Total PCBs Total PAHs	One flow proportional composite sample over duration of selected wet-weather events. Please see Section 4.2 for further details.

Table 4.3 Storm-Borne Sediment

TMDL	Target Analyses	Monitoring Frequency
BC Estuary Toxics	Cadmium Copper Lead Silver Zinc DDTs Chlordane Dieldrin Total PCBs Total PAHs	Annually, utilizing a flow-proportioned composite sample consisting of sediment from each storm event.

Table 4.4 Sediment Quality

Target Analyses		Monitoring Frequency
Cadmium	Dieldrin	Semi-annually during first year, annually thereafter.
Copper	Total PCBs	
Lead	Total PAHs	
Silver	Total Organic Carbon (TOC)	
Zinc	Grain Size	
Chlordane	Sediment Toxicity	
DDTs		

Table 4.5 Bioaccumulation

Target Analyses		Monitoring Frequency
None are specified in the TMDL. The following list of target analyses is proposed.		The monitoring frequency is not specified; therefore annual monitor will be conducted.
Cadmium	Chlordane	
Copper	DDTs	
Lead	Dieldrin	
Silver	Total PCBs	
Zinc	Total PAHs	

4.2 Sampling Procedures

Detailed sampling standard operating procedures are included in Appendix D.

During dry-weather grab samples will be utilized for water quality monitoring. Samples will be collected monthly at the locations described previously.

Automatic samplers will be utilized to collect samples during wet-weather events. Initially, automatic samplers will only be installed at the four (4) Tier I locations. Samplers will only be installed at specific Tier II locations when predicated by the data from the upstream Tier I sites. As specified in the Metals TMDL, wet weather is defined as a flow in Ballona Creek of greater than 40 cubic feet per second. For the purposes of this TMDL, flow will be measured at Site BC-2, the historical LA County mass emission station. Each sampler will be programmed to utilize information from an on-board flow meter to collect flow-proportional composite samples. To the extent possible, samples will be collected over the entire duration of the storm. A minimum of 72 hours after a storm is needed to service and set up the auto samplers; therefore, no sampling will be done when the second of two consecutive storms starts within 72 hours of the end of the first. No more than 24 storms will be sampled per year.

Prior to the start of the effectiveness monitoring period, a pilot study will be initiated to collect storm-borne sediment samples from the storm water samples collected during

each storm event. Approximately 50 grams of storm-borne sediment will be required to perform the analyses required by the Estuary TMDL. Based on an average total suspended solids (TSS) concentration of 560 mg/L (LA County data from 2004-2005), approximately 25 gallons of stormwater will be required to capture this amount of sample. The actual amount of stormwater needed, which will vary with its actual TSS, could be significantly greater than 25 gallons. The feasibility of combining storm-borne sediments from an entire season of storms in proportion to storm water flow to create an annual storm-borne sediment sample will be investigated. If this approach is determined to be unfeasible, the Jurisdictional Group will propose an alternative to the RWQCB.

Depending upon location sediment grab samples will be collected from a boat or on-foot. Sediment sampling from a boat will be done with a "Ponar grab"; sampling by direct (foot) access will be done by hand.

Bioaccumulation sampling techniques may vary due to season, weather, flow rate, target species, etcetera. Sport fish may be taken by hook and line or seine. Mussels will be collected by hand. Sport fish must meet minimum size requirements of CDFG sport fishing regulations in order to be assessed for human health concerns.

Five individuals of both fish and mussel will be collected and analyzed from each of the two sampling sites (2 and 4). Muscle tissue will be analyzed for fish and the entire body will be used for the mussel analyses. Individuals should be analyzed separately to show/learn variation within the species sampled and the sample location.

4.3 Sampling Equipment

Equipment and supplies needed for shoreline sample collection are listed in Appendix C.

4.4 Field and Laboratory Safety

In an effort to improve employee safety and health awareness and prevent occupational-related injury and illness, the EMD and other participating laboratories have developed a safety program with the intention of satisfying the applicable federal, state, and local regulations. For example, EMD's Safety and Health Program is composed of specific elements required by Cal/OSHA General Industry Safety Order Section 5191: Occupational Exposure to Hazardous Chemicals in Laboratories, and section 3203: The Injury and Illness Prevention Program, and any other applicable regulations. The written safety plan, titled ***The Chemical Hygiene Plan***, is available to all employees for review and should be recognized as management's commitment to ensure that all employees carry out their work in the safest and most efficient manner possible. The EMD employees will be kept familiar with the division's written Chemical Hygiene Plan (CHP) through training, annual review, and monthly staff safety meetings.

It is EMD's policy and the policy of other participating agencies to have a safe working environment for all of its employees and that all field and laboratory work be performed

in a manner that provides the highest level of safety for the protection of every employee. See Appendix M for detailed safety protocols.

4.5 Analytical Methodology

The analytical methodologies, for the various monitoring programs covered by this CMP, are tabulated below in Table 4.6. The water quality analyses for metals will use EPA Method 200.7 (ICP) versus EPA Method 200.8 (ICP-MS) and monitor only for total recoverable metals and not dissolved metals. Even though dissolved metal sampling was recommended as part of the ambient monitoring program, the WLAs for the TMDL are only based on total recoverable metals. Therefore, the responsible agencies have decided to only sample for total recoverable metals. The agencies may pursue a special study to verify the translators used for this TMDL and will sample for the dissolved metals at that time.

Table 4.6 Water Quality Methods

TMDL	Analyses	Analytical Methodology*
BC Metals	Hardness	Standard Methods 20th Edition, Method 2340
	Selenium	EPA 200.7
	Copper, Lead, & Zinc	EPA 200.7
BC Estuary Toxics	Cadmium, Copper, Lead, Silver, & Zinc	EPA 200.7
	DDTs, Chlordane, Dieldrin, & Total PCBs	EPA 608
	Total PAHs	EPA 625

* Detailed Standard Operating Procedures for these methods can be found in Appendix F.

Table 4.7 Storm-Borne Sediment Methods

TMDL	Analyses	Analytical Methodology*
BC Estuary Toxics	Total Suspended Solids	Standard Methods 20th Edition, Method 2540D
	Total Dissolved Solids	Standard Methods 20th Edition, Method
	Settleable Solids	Standard Methods 20th Edition, Method
	Total Organic Carbon	Standard Methods 20th Edition, Method
	Cadmium, Copper, Lead, Silver, & Zinc	EPA 6010
	DDTs, Chlordane, Dieldrin, & Total PCBs	EPA 8081 & 8082
	Total PAHs	EPA 8270

* Detailed Standard Operating Procedures for these methods can be found in Appendix F.

Table 4.8 Sediment Quality Methods

TMDL	Analyses	Analytical Methodology*
BC Estuary Toxics	Sediment Toxicity	
	Grain Size	EMD SOP #4160
	Total Organic Carbon	Standard Methods 20th Edition, Method
	Cadmium, Copper, Lead, Silver, & Zinc	EPA 6010
	DDTs, Chlordane, Dieldrin, & Total PCBs	EPA 8081 & 8082
	Total PAHs	EPA 8270

* Detailed Standard Operating Procedures for these methods can be found in Appendix F.

Ballona Creek Estuary Toxics TMDL: Sediment Toxicity Testing

Two types of sediment toxicity monitoring are required in the Ballona Creek Estuary Toxics TMDL: Ambient monitoring and Effectiveness monitoring. Ambient monitoring is the collection of background water quality data to set numeric targets and waste load allocations and assist in the implementation of BMPs. Effectiveness monitoring will measure the water quality throughout Ballona Creek and assess the progress being made to remove the toxic components in the La Ballona Creek Estuary sediments.

The City of Los Angeles, Environmental Monitoring Division (CLA EMD) ambient monitoring sediment toxicity testing program shall consist of six stations, analyzed semi-

annually in the first year of the TMDL (baseline) and then annually to evaluate the BMPs until the TMDL is reopened in the sixth year. The sediment testing will consist of both acute and chronic tests and will utilize three marine organisms; 28-day chronic and a10-day acute amphipod mortality test; pore water testing utilizing the sea urchin fertilization test; and the testing of overlying water using the red abalone larval development test. The chronic 28-day and the acute 10-day amphipod tests will be compared in the initial year of semi-annual testing and if there is no significant difference between the results of the two tests, the 10-day test will be used throughout the rest of the monitoring. If the sediment samples contain insufficient pore water to conduct sea urchin fertilization tests a chronic polychaete mortality test will be substituted.

Effectiveness sediment toxicity test monitoring will be conducted semi-annually on six sites and shall consist of the same sediment toxicity tests selected for the ambient monitoring program. Toxic sediment will be identified by an average amphipod survival of 70% of less. Accelerated monitoring will consist of six additional tests conducted approximately two weeks between the termination of one test and the initiation of the next. This will allow the purchase of test organisms, the equipment preparation, and the analysis of test results to be completed prior to the start of the next accelerated test. If no exceedances occur during the six accelerated test samples then regular monitoring will resume. If any two of the accelerated tests have less than an average of 90% survival then an investigation into the cause of the toxicity shall be implemented (i.e. TIE). This investigation may include the testing of the sediment pore water, sediment overlying water, or the manipulation of sediment by physical or chemical means. If no reduction in toxicity can be accomplished with the available technology then the investigation will cease until further direction from the Regional Water Quality Control Board. Both accelerated monitoring and the toxicity investigation shall be initiated in the fiscal year succeeding the exceedance. This will allow the City of Los Angeles and the adjoining jurisdictions to budget sufficient funding for the additional testing.

Table 4.9 Bioaccumulation Methods

TMDL	Target Analyses	Analytical Methodology*
BC Estuary Toxics	Cadmium, Copper, Lead, Silver, & Zinc	EPA 6010
	DDTs, Chlordane, Dieldrin, & Total PCBs	EPA 8081 & 8082
	Total PAHs	EPA 8270

* Detailed Standard Operating Procedures for these methods can be found in Appendix F.

All laboratories performing analyses for TMDL monitoring shall maintain Environmental Laboratory Accreditation Program certification (ELAP administered by California Department of Health Services) for specified methods from the following ELAP Fields of Testing; # 108 – Inorganic Chemistry of Wastewater, # 109 Toxic Chemical Elements of Wastewater, # 111 Semi-Volatile Organic Chemistry of Wastewater, #114 Inorganic Chemistry of Hazardous Waste, and # 117 Semi-Volatile Organic Chemistry of

Hazardous Waste. Additionally, all laboratories shall submit detailed SOPs for review by Regional Board staff. Appendix F provides examples of SOPs developed by the City of Los Angeles-EMD. Each analytical method used for the TMDL monitoring program shall be an approved EPA or Standard Methods for the Examination of Water and Wastewater, 18th-20th edition (APHA 1992-98) method. Laboratories receiving Regional Board approval may use other analytical methods for TMDL monitoring.

4.6 Quality Assurance/Quality Control

All laboratories must employ a program that associates quality assurance with the laboratory facility, staff, instrumentation and equipment, materials and methods, reagents, and data validation. These QA/QC measures may be included in the submitted SOPs or defined in a separate QA/QC document such as Appendix H. The quality assurance procedures shall be in accordance with Standard Methods for the Examination of Water and Wastewater, 18-20th Editions (APHA 1992-98). All participating laboratories must maintain ELAP certification, and provide QA/QC documentation as required by the Regional Board.

4.7 Data Management and Reporting

All data collected will be archived within the City of Los Angeles' Bureau of Sanitation database. Non-City of Los Angeles monitoring agencies performing analyses for this program will submit their data to the Bureau electronically on an annual basis. Sanitation staff will ensure electronic submissions of data are parsed and stored correctly into its database.

Copies of the annual reports will be distributed to the responsible agencies prior to submittal to the Regional Board for review and approval. The final summary reports will be submitted to the Regional Water Quality Control Board on an annual basis along with compliance summary tables. See Appendix G for data acquisition, reduction, validation, and reporting SOPs.

5.0 LITERATURE CITED

1. American Public Health Association (1992-98). Standard Methods for the Examination of Water and Wastewater, 18th-20th ed. APHA, AWWA, WPCF, Washington, D.C.

2. Test Methods for Evaluating Solid Waste. 1986. Revision December 4, 1996. Volume IB: Laboratory Manual Physical/Chemical Methods, 3rd Edition. United States Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, D.C.

3. TMDL Drafts from California Regional Water Quality Control Board, Los Angeles Region and U.S. EPA, Region 9, are as follows:

   Total Maximum Daily Load for Metals in Ballona Creek. July 7, 2005.

   Total Maximum Daily Load for Toxic Pollutants in Ballona Creek Estuary. July 7, 2005.

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APPENDICES

APPENDIX A

Development History of Ballona Creek Metals & Ballona Creek Estuary Toxic Pollutants TMDLs

In December 1997, the Natural Resources Defense Council (NRDC), acting as legal representative for Heal the Bay, Inc., and Santa Monica BayKeeper, Inc., filed a Notice of Intent to sue the United States Environmental Protection Agency (USEPA) over failure of the Regional Water Quality Control Board, Los Angeles (LARWQCB), to adequately implement the 303(d)/TMDL Program. In December 1998, NRDC and BayKeeper entered into a Federal Consent Decree with EPA. The Consent Decree established 92 TMDL analytical units, which are water quality limited segments and associated pollutants for which TMDLs must be developed. Specific dates were established for development of some of these TMDL analytical units. The Ballona Creek Metals TMDL (Creek) analytical unit (57) had a required completion date of March 22, 2005 for the Regional Board. The Ballona Creek Estuary Toxics TMDL (Estuary) analytical units (55 & 57) had a required completion date of March 22, 2005 for the Regional Board. USPEA and the consent decree plaintiffs agreed to extend the completion deadline for the Creek and Estuary TMDLs to January 11, 2007. A California Environmental Quality Act (CEQA) Scoping Meeting was conducted by the Regional Board, on June 12, 2003, to consult with the public and interested stakeholders about the environmental effects of the preliminary drafts of the TMDLs. The TMDLs were approved by the USEPA and became effective January 11, 2006. The TMDLs require the responsible jurisdictions and responsible agencies to submit a coordinated monitoring plan within 12 months after the effective date.

Ballona Creek was designated as impaired and included on California's 2002 CWA §303(d) list of impaired waters due to excessive amounts of copper, lead, selenium, and zinc. Ballona Creek Estuary was designated as impaired and included on California's 1998 CWA §303(d) list of impaired waters due to excessive amounts of cadmium, copper, lead, silver, zinc, chlordane, total DDT, total PAH, and total PCBs.

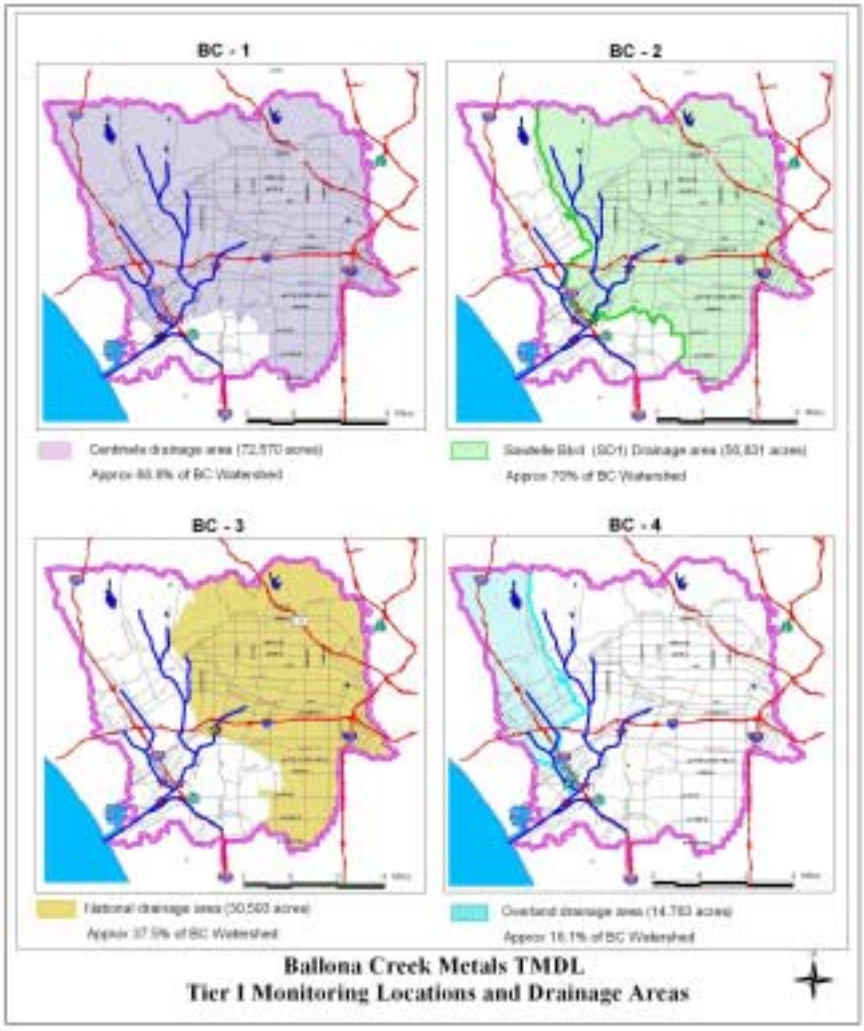
The Ballona Creek Metals and Estuary Toxics TMDL Group was formed in October 2005. Representatives from California State Department of Transportation, Los Angeles County Department of Public Works (LADPW), City of Los Angeles Bureau of Sanitation (CLABOS), Beverly Hills, Culver City, Inglewood, and Santa Monica were in attendance. Work was quickly initiated on the Monitoring Plan that was due on January 11, 2007. Preliminary discussions of the Implementation Plan also began at this time.

APPENDIX B

Ballona Creek Metals TMDL Water Quality Monitoring Locations and Ballona Creek Estuary Toxics TMDL Stormwater Quality and Storm-Borne Sediment Monitoring Locations

Table 1. Tier I - Effectiveness Locations

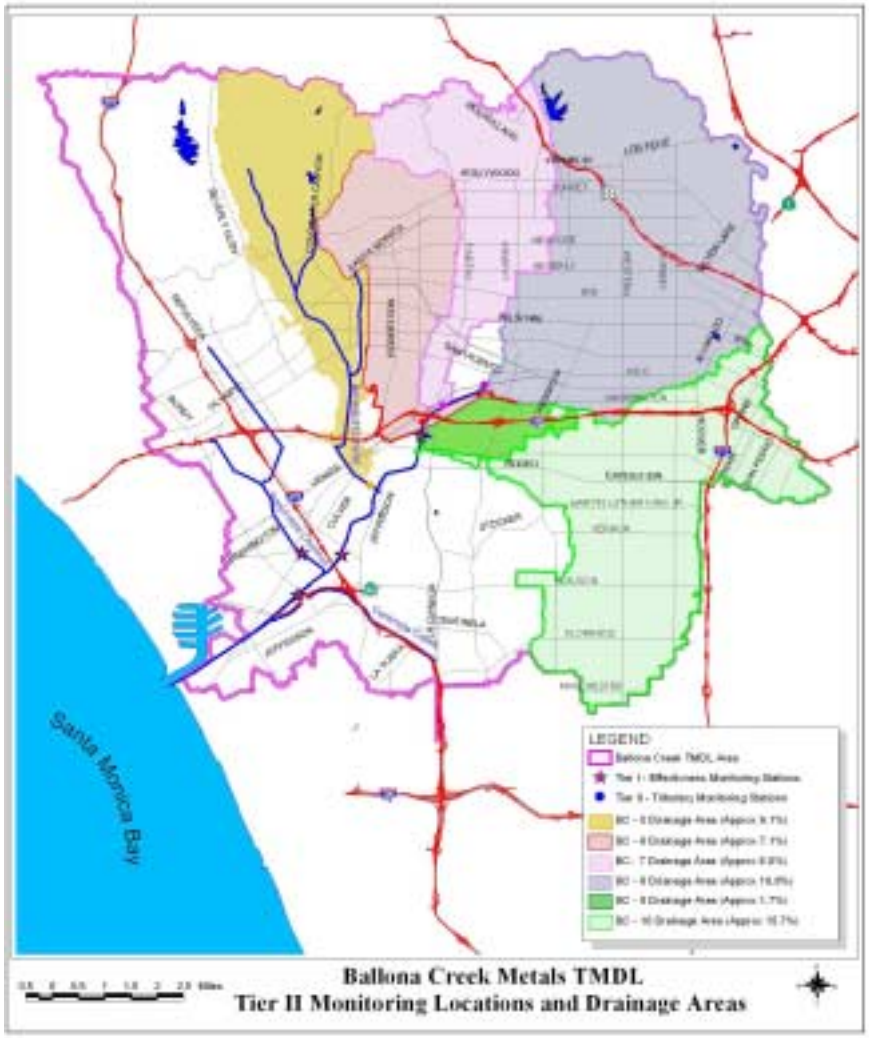
Monitoring Location	TMDL Addressed	Reach	Location	Freq	Lat.	Long.	Thomas Guide Coordinates	Percentage of Watershed	Comments
BC - 1	Both	2	Main Channel	Monthly	33.986	118.415	672:E6	88.8%	At Centinela Ave over crossing of main channel
BC – 2	Both	2	Main Channel	Monthly	34.996	118.402	672:F5	70.0%	At Sawtelle Blvd over crossing of main channel (LACDPW – S01)
BC - 3	Both	1	Main Channel	Monthly	34.026	118.376	632:J7	37.5%	At National Blvd over crossing of main channel
BC – 4	Both	2	Tributary	Monthly	33.997	118.415	672:E4	18.1%	Just above the confluence w/ Ballona Creek (Sepulveda Channel)


BC - 1
BC - 2
BC - 3
BC - 4
Ballona Creek Metals TMDL
Tier I Monitoring Locations and Drainage Areas

Ballona Creek Metals TMDL Water Quality Monitoring Locations and Ballona Creek Estuary Toxics TMDL Stormwater Quality and Storm Borne Sediment Monitoring Locations

Table 2. Tier II – Upstream Locations

Monitoring Location	TMDL Addressed	Reach	Location	Freq	Lat.	Long.	Thomas Guide Coordinates	Percent of Watershed	Comments
BC – 5	Both	2	Tributary	Monthly	34.017	118.389	672:H2	9.1%	Just above the confluence w/ Ballona Creek (Benedict Canyon)
BC – 6	Both	1	Tributary	Monthly	34.032	118.375		7.1%	Just before entering Ballona Creek (near La Cienega)
BC – 7	Both	1	Tributary	Monthly	34.038	118.368	633:A6	8.0%	Just before entering Ballona Creek (near Fairfax Ave)
BC – 8	Both	1	Tributary	Monthly	34.044	118.353	633:C5	19.8%	Beginning of where Ballona Creek daylights (near Cochran)
BC – 9	Both	1	Tributary	Monthly	34.029	118.375	633:A7	1.7%	Just before entering Ballona Creek (near Adams)
BC -10	Both	2	Tributary	Monthly	34.026	118.376	632:J7	15.7%	Just before entering Ballona Creek (near Jefferson Blvd)


Santa Monica Bay
LEGEND:
Ballona Creek Metals TMDL
Tier II Monitoring Locations and Drainage Areas

Ballona Creek Estuary Toxic Pollutants TMDL
Monitoring Locations

Sediment

Table 3. Sediment Monitoring Locations

Monitoring Location	TMDL Addressed	Reach	Location	Freq*	Lat.	Long.	Comments
BCE – 1	Toxics	3	Estuary	See Note 1	33.960	118.459	This is a historical station located at the mouth of Ballona Creek.
BCE – 2	Toxics	3	Estuary	See Note 1	33.963	118.454	This is a fixed selected sampling site, located at the Pacific Street Bridge.
BCE – 3	Toxics	3	Estuary	See Note 1	TBD	TBD	This is a randomly selected sampling site, located between the Pacific Street Bridge and the Ballona Wetlands self regulating tide gate.
BCE – 4	Toxics	3	Estuary	See Note 1	TBD	TBD	This is a randomly selected sampling site, located between the Ballona wetlands tide-gate and Culver Blvd.
BCE – 5	Toxics	3	Estuary	See Note 1	TBD	TBD	This is a randomly selected sampling site, located between the Centinella Creek and Culver Blvd.
BCE – 6	Toxics	3	Estuary	See Note 1	TBD	TBD	This is a randomly chosen station, located between the confluence with Centinela Creek and the upper boundary of the Ballona Creek

Note 1: Sediment samples will be taken semiannually for the first year and annually thereafter.

Bioassessment

Table 4. Bioaccumulation Monitoring Locations.

Monitoring Location	TMDL Addressed	Reach	Location	Freq	Lat.	Long.	Comments
BCE – 1	Toxics	3	Estuary	See Note 2	33.960	118.459	This is a historical station located at the mouth of Ballona Creek. Mussels targeted.
BCE – 2	Toxics	3	Estuary	See Note 2	33.963	118.454	This is a fixed selected sampling site, located at the Pacific Street Bridge. Both mussels and fish targeted.
BCE – 3	Toxics	3	Estuary	See Note 2	TBD	TBD	This is a randomly selected sampling site, located between the Pacific Street Bridge and the Ballona Wetlands self regulating tide gate. Mussels targeted.
BCE – 4	Toxics	3	Estuary	See Note 2	TBD	TBD	This is a randomly selected sampling site, located between the Ballona wetlands tide-gate and Culver Blvd. Both mussels and fish targeted.

Note 2: Bioaccumulation samples will be taken annually.

APPENDIX C

Field Sampling Equipment and Supply List

The following equipment is needed for dry weather water quality sample collection.

1. First Aid kit
2. Portable eyewash bottle with saline solution
3. Ice chest (with ice)
4. Sampling pole with reel
5. Weighted bottle holder (attaches to fishing line/reel)
6. Nalgene 1-liter sample bottles, acid-washed
7. Nalgene 500-mL sample bottles, acid-washed (for sampling low-flow streams)
8. Wash bottle with de-ionized water
9. Foaming disinfectant hand cleanser
10. Waterproof labels
11. Paper towels
12. Water-safe pen and Lab marker
13. Field log sheet
14. Chain-of-Custody (COC) sheet
15. Thomas Guide (street map)
16. Trash bag
17. Cell phones (1 for each person)
18. Personal protective equipment:
    i. Safety vest (ANSI 107 Class 2 compliant, high visibility)
    ii. Protective gloves (latex, nitrile, etc.)
    iii. Slip-resistant shoes/boots
    iv. Protective eyewear: UV protection; impact resistant
    v. Foul weather gear (when necessary)
    vi. Rain boots (when necessary)
    vii. Life vest (if entering the flood channel).

APPENDIX D

Sampling Standard Operating Procedures

Dry Weather Water Quality Sampling

Overview of Procedure

At the beginning of each month, Field Sampling staff provides Laboratory Staff at the Environmental Monitoring Division (EMD) with a sampling schedule which details when sampling will be conducted, and the number of samples to be delivered. If "dry-weather" criteria (listed above) are not met, sampling is postponed until the next convenient "dry-weather" day, and Laboratory staff is notified of the change. The Laboratory supplies Field Sampling staff with clean, acid-washed bottles. Sample bottles are labeled and Chain-of-Custody (COC) sheets are prepared prior to going out to the field. All necessary gear, including personal protective equipment, must be brought to the field. Grab samples are collected at designated sampling stations, and the time of collection is recorded on the COC sheets and Field Log Sheet. Samples are then stored on ice, and delivered to the Sample Receiving window at the Environmental Monitoring Division (5th floor, Pregerson Building). Laboratory staff is reminded that samples need to have preservative (Nitric Acid) added to the sample bottles. The original COC sheet is signed and given to EMD staff. The Field Sampling crew retains a copy of the COC.

I. Safety

A. Be Alert: Always be aware of potentially hazardous situations. Exercise common sense when you encounter suspicious persons or animals. Your personal safety is your first responsibility. Never place yourself in a dangerous or unsafe situation.

B. Traffic: Always be mindful of traffic conditions. Always wear high-visibility clothing (ANSI 107 Class 2) when sampling near areas open to vehicular traffic. Never sample in traffic conditions that you feel are unsafe. Never attempt to setup a traffic-stop without the proper equipment and training.

C. Always wear protective gloves and eyewear when collecting water samples. Avoid water contact with eyes and skin. If accidental contact with eyes occurs, use portable eyewash bottles as directed. Wash hands thoroughly after collecting samples.

D. Always wear chemical-resistant, slip-resistant shoes when collecting samples.

E. Never enter the flood channel when there is high flow or during rainy conditions. Never stand or walk in moving water. Never get too close to the low-flow channel.

F. Never enter an enclosed drain, tunnel, or confined space. These spaces can become devoid of oxygen/air and you can suffocate.

G. Never sample alone. At least two people must be present at all times. Take communication equipment (cell phones) with you to report any accidents, seek assistance, or maintain contact with your partner.

II. Sampling Procedure

A. Coordination with Laboratory.

At the beginning of each month, the monthly sampling schedule is sent via email to the supervisors of the Inorganic Chemistry Section and Data/Sample Management Section at EMD. If unforeseen changes are made to the schedule, EMD staff is notified immediately. Contact names are listed below:

Inorganic Chemistry Section

Supervisor: Soun Chanjamsri

Phone: (310) 648-5995

Email: soun.chanajamsri@lacity.org

Data/Sample Management Section

Supervisor: Susan Chang

Phone: (310) 648-5607

Email: susan.chang@lacity.org

B. Gather the necessary equipment

1. First Aid kit
2. Portable eyewash bottle with saline solution
3. Ice chest (with ice)
4. Sampling pole with reel
5. Weighted bottle holder (attaches to fishing line/reel)
6. Nalgene 1-liter sample bottles, acid-washed
7. Nalgene 500-mL sample bottles, acid-washed (for sampling low-flow streams)
8. Wash bottle with de-ionized water
9. Foaming disinfectant hand cleanser
10. Waterproof labels
11. Paper towels
12. Water-safe pen and Lab marker
13. Field log sheet
14. Chain-of-Custody (COC) sheet
15. Thomas Guide (street map)
16. Trash bag
17. Cell phones (1 for each person)

18. Personal protective equipment:
    i. Safety vest (ANSI 107 Class 2 compliant, high visibility)
    ii. Protective gloves (latex, nitrile, etc.)
    iii. Slip-resistant shoes/boots
    iv. Protective eyewear: UV protection; impact resistant
    v. Foul weather gear (when necessary)
    vi. Rain boots (when necessary)
    vii. Life vest (if entering the flood channel).

C. Sampling Locations:
The 12 Tier I and Tier II sampling stations are listed in the table below. Prior to sampling, confirm which stations are to be sampled (Tier I vs. Tier II).

Station ID		Waterbody	Location	Thomas Guide Coordinates
Tier I	BC-01	Main Channel: Ballona Creek	Inglewood Blvd.	672:E6
	BC-02	Main Channel: Ballona Creek	Sawtelle Blvd.	672:F5
	BC-03	Main Channel: Ballona Creek	National Blvd.	632:J7
	BC-04	Tributary: Sepulveda Channel	Culver Blvd.	672:E4
Tier II	BC-05	Tributary: Benedict Canyon	Duquesne Ave.	672:H2
	BC-06	Tributary: Fairfax	La Cienega	
	BC-07	Tributary: Fairfax	Fairfax Ave.	633:A6
	BC-08	Main Channel: Ballona Creek	Cochran Ave.	633:C5
	BC-09	Tributary: Adams	Adams Ave.	633:A7
	BC-10	Tributary: Drain #84	Jefferson Blvd.	632:J7

D. Field Log sheet.
A field log sheet is provided in Appendix 2. This form is for recording details about each sampling event (including Date, time, locations, samplers,

comments), and is retained by the sampling staff. The form is to be prepared before leaving to the field, and the appropriate information is filled out after each sample is collected.

E. Chain of Custody (COC) form.
A COC form is to be completed for each sampling event. The form should be prepared prior to leaving to the field. At each sampling station, the sampler enters his/her initials, along with time of collection. The original COC is to follow the samples at all times. The sampler must sign and date the COC when relinquishing the sample to Laboratory Staff (Sample Receiving, EMD) who in turn, signs the form to indicate receipt of the sample. A photocopy is given to the sampling staff, and the laboratory retains the original COC along with the samples to be analyzed. A blank COC is provided in Appendix 3.

F. Collecting Samples
When sampling from a bridge, a fishing pole/reel is used to lower the sample bottle into the stream.
    a. Obtain a clean, acid-washed bottle (1Liter, plastic nalgene). Confirm that the bottle has the appropriate pre-printed label. If the depth of the water is low, it may be necessary to collect multiple samples using a smaller bottle (500 mL), and compositing sub-samples until a volume of 1 Liter is obtained.
    b. Note the sample collection time on the Field Log sheet, COC, and sample label.
    c. Be very careful to avoid contamination of the sample bottle. Avoid touching the mouth of the bottle and the inside of the cap.
    d. Attach the bottle-holder to the fishing line, and secure the bottle. Unscrew the bottle lid, and set it aside. Release the drag on the reel, and lower the bottle into the stream. Allow the bottle to fill with water, and then reel it in. Replace the lid securely, and place the sample into the ice chest.
    e. Rinse bottle holder with de-ionized water after each station.
    f. Fill in appropriate information on the COC and field log sheet.
    g. Samples should be delivered to the laboratory as soon as possible. When relinquishing custody of the samples, inform Laboratory staff that samples need to have preservative added (this should also be indicated on the COC). Sign and date the COC, and obtain a copy after the laboratory staff member has signed the original.
    h. Upon returning from the field, file the COC (copy) and field log sheet in the appropriate binder. Rinse all field equipment with de-ionized water.

III. Contact Information:

Laboratory:

Data/Sample Management

- Supervisor: Susan Chang
  Phone: (310) 648-5607
  Email: susan.chang@lacity.org

- Sample Receiving Desk
  Phone: (310) 648-5831

Inorganic Laboratory (Metals)

- Supervisor: Soun Chanjamsri
  Phone: (310) 648-5995
  Email: soun.chanajamsri@lacity.org

Recipients of lab results:

Watershed Protection Division:

- Pollution Assessment Section
  Supervisor: Vivian Marquez
  Phone: (323) 342-1556
  Email: vivianmarquez@lacity.org

- TMDL Implementation Section
  Supervisor: Wing Tam
  Phone: (213) 485-3985
  email: wing.tam@lacity.org

Wet Weather Water Quality and Storm-Borne Sediment Sampling

Wet weather water sampling

Flow-weighted composite samples will be collected to obtain the representative sample for each storm event. This sampling method is currently used for the storm water monitoring required by Los Angeles County's NPDES permit. A flow-weighted composite sample is obtained by mixing a series of discrete samples (aliquots) of specific volume, collected at specific runoff volume intervals over the duration of the storm event. The concentration of the sample is called Event Mean Concentration (EMC).

An automatic sampler will be programmed to start automatically when the water level in the channel or storm drain exceeded a certain height such that the corresponding flow rate exceeded a pre-determined wet weather flow rate at the sampling location. Samples will be retrieved from the automated samplers as soon as possible to meet laboratory analysis holding time requirements. As samples were collected, rainfall and runoff data were logged and stored for transfer to the office. The automated sampler will be programmed with the intent of capturing the major portion of a runoff event.

a) Wet weather water data per metals TMDL

The metals load at each monitoring site will be estimated by multiplying the EMC by the total runoff volume measured at the site. The total runoff volume can be calculated based on the runoff hydrograph that would be generated over the entire storm duration by the continuous measurements of flow rate by the automatic samplers. Similarly, the daily metal load can be calculated by multiplying the daily runoff volume the EMC.

b) Wet weather water data per estuary toxics TMDL

Similarly to the metal load measurement method, the toxics load in the storm water at the estuary will be estimated by multiplying the EMC by the total runoff volume measured at the site. The loads from each storm event will be summed for the entire year to yield total load for the year.

c) Wet weather sediment data per estuary toxics TMDL

Sediment collected from each wet-weather event that is sampled will be saved. Freezing will be used to preserve these sediment aliquots. After the end of the wet-weather season the aliquots will be combined to create a storm flow proportioned composite sample that will be analyzed for the TMDL required constituents. Prior to

the start of the effectiveness monitoring program, this sampling scheme will be employed at a limited number of sites to test its utility. If this sample collection scheme cannot be practically applied, other approaches will be explored.

QA & QC

Sampling methodology

Properly performed monitoring station set up, water sample collection, sample transport, and laboratory analyses are vital to the collection of accurate data. Quality Assurance/Quality Control (QA/QC) is an essential component of the monitoring program.

Evaluation of Analytes and QA/QC Specifications for Monitoring Program (Woodward-Clyde 1996a) and *Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to West Coast Marine and Estuarine Organisms* (USEPA 1995) describe the procedures used for bottle labeling, chain-of-custody tracking, sampler equipment checkout and setup, sample collection, field blanks to assess field contamination, field duplicate samples, and transportation to the laboratory.

An important part of the QA/QC Plan is the continued education of all field personnel. Field personnel will be adequately trained from the onset and informed about new information on storm water sampling techniques on a continuing basis. Field personnel also evaluate the field activities required by the QA/QC Plan, and the Plan is updated if necessary.

- Bottle Preparation

For each monitoring station, a minimum of three sets of bottles will be available so that up to two complete bottle change-outs could be made for each storm event. Bottle labels contained the following information:

- Sample ID Number
- Station Number
- Station Name
- Sample Type (Grab or Composite)
- Laboratory Analysis Requested
- Date
- Time
- Preservative
- Temperature
- Sampler's Name

Bottles will be cleaned at the laboratory prior to use, then they will be labeled and stored in sets. Each station will be provided with the same number, types, and

volumes of bottles for each rotation. Clean composite sample bottles will be placed in the automated sampler when samples are collected. This practice ensures readiness for the next storm event. All bottles currently not in use are stored and later transported in plastic ice chests. Composite sample bottles are limited to a maximum of 2.5 gallons each, to ensure ease of handling.

- Chain-of-Custody Procedure

Chain-of-custody forms will be completed to ensure and document sample integrity. These procedures establish a written record which tracks sample possession from collection through analysis.

- Field Setup Procedures

All field-sampling locations will be fixed sites, with the automated sampler placed on a public road or flood control right-of-way. After sample collection, field staff will prepare the sampler for collection of the next set of samples. Inspection of visible hoses and cables will be performed to ensure proper working conditions according to the site design. Inspection of the automatic sampler and appurtenances including strainer, pressure transducer, and auxiliary pump will be performed during daylight hours in non-storm conditions. The automated sampler will be checked at the beginning of the storm to ensure proper working condition and to see if flow composite samples are being collected properly.

Bottles will be collected after each event and packed with ice and foam insulation inside individually marked ice chests. Chain-of-custody forms will be completed by field staff before transportation of the samples to the laboratory. Under no circumstance will the samples be removed from the ice chest during transport from the field to the laboratory.

- Travel Blanks and Field Duplicates

Potential field contamination will be assessed through analysis of travel blanks and duplicate grab samples. Field travel blanks will be collected for each monitoring station during every sampling event to quantify post-sampling contamination. The monitoring program also includes field duplicates to assess the precision of laboratory results. A field duplicate, the origin of which is unknown to the laboratory, will be collected for each sampling event. This methodology for assessing post-sampling contamination and laboratory testing procedures provided data to measure the precision and accuracy of the laboratory results.

Sediment and Bioaccumulation Sampling

Ballona Creek Estuary Sediment Sampling

The sediment sampling methodology in the Ballona Creek Estuary should follow the same guidelines/protocols as used in Santa Monica Bay offshore monitoring and Regional Monitoring for comparative purposes.

EMD proposes six sediment sites in the estuary:

1. BCE-1 (33º57.607 N 118º27.548 W) is located at the mouth of Ballona Creek Estuary. This is a "historical station" with existing data the Bay Protection and Toxic Cleanup Program (BPTCP: Station 44014.0) in 1993 which can be used to determine temporal trends in pollutant concentrations
2. BCE-2 (33º57.769 N 118º27.235 W) is located at the Pacific Street Bridge. This site has the highest human contact, swimming, fishing (taking of fish, crabs, and mussels), kayaking, etc.
3. BCE-3 is a randomly chosen station, located between the Pacific Street Bridge and the Ballona wetlands tide-gate.
4. BCE-4 is a randomly chosen station, located between the Ballona wetlands tide-gate and Culver Blvd.
5. BCE-5 is a randomly chosen station, located between Culver Blvd and the confluence with Centinela Creek.
6. BCE-6 is a randomly chosen station, located between the confluence with Centinela Creek and the upper boundary of the Ballona Creek Estuary.

Sediment sampling from a boat will be done with a "Ponar grab"; sampling by direct (foot) access will be done by hand. The top 2 centimeters of sediment will be sampled with a Teflon scoop and placed in the appropriate containers. Good faith efforts will be made to collect representative samples from each of the six locations. If samples cannot be obtained from the exact sample point, a reasonable attempt will be made to collect a sample from the vicinity of the sample point. If this proves unsuccessful, no sample will be collected from the given sample point. If samples cannot be collected during two consecutive sampling events, alternate sampling point(s) will be proposed to the RWQCB.

sample type	container	volume
Grain size	8oz. plastic	7/8 full (airspace)
TOC	4oz. glass	7/8 full (airspace)
Metals (copper, cadmium, lead, silver, zinc)	4oz. plastic	7/8 full (airspace)
Organics (DDT, PCBs, PAHs, chlordane)	4oz. plastic	7/8 full (airspace)

Sediment monitoring for TOC, grain size, metals and organics will be done semiannually for first year of the TMDL, then annually to evaluate effectiveness until the sixth year in order to reconsider effectiveness.

Ballona Creek Estuary Bioaccumulation Sampling

Data from two bioaccumulation sampling sites, at BCE-2 and BCE-4 (see above) will be used to monitor trends in the concentration of contaminants in the tissues of aquatic organisms. This will be conducted in order to assess both ecological and human health concerns and to see if the trends or patterns of contaminant concentrations mirror that observed from the sediment analyses. Human health concerns will be assessed by sampling the tissues from fish species that are commonly taken for consumption by sport fisherman. Reasonable attempts will be made to collect two to three species of sport fish; but, if sport cannot be obtained, whatever species of fish, if any, that can be obtained will be used.

Sampling techniques may vary due to season, weather, flow rate, target species, etc. Sport fish may be taken by hook and line or seine. Mussels will be collected by hand. Sport fish must meet minimum size requirements of Calif. Fish and Game sport fishing regulations in order to assess for human health concerns. If possible, sport fish species that are subject to human consumption will be targeted. Should station location prohibit taking of sport fish, then any practical alternative fish species present will be used.

Tissues will be analyzed for Chlordane, DDT, PCBs, and PAHs.

Five individuals of both fish and mussel will be collected and analyzed from each sampling site. Muscle tissue will be analyzed for fish and the entire body will be used for the mussel analyses. Individuals will be analyzed separately to show/learn variation within the species sampled and the sample location.

Sampling will be semiannual the first year and results of the initial sampling will be assessed to determine frequency and number (individual vs. composite) of future bioaccumulation sampling and the effectiveness.

APPENDIX E

EMD Chain-of-Custody Form

Examples of worksheets for Chain of Custody sheets (next 2 pages) used by the City of Los Angeles' Environmental Monitoring Division are provided herein.

Date:

Department of Public Works
Bureau of Sanitation
Environmental Monitoring Division

Sample Chain of Custody

EMD
LIMS #: _____

EMD Sample ID: _____
Project Name: _____

Sampling Information:
Sampling Agency: _____
Agency Sample ID#: _____
Phone Number: _____
Fax Number: _____
Contact Person: _____
email address: _____

Sampler's Name: _____
Sampler's Title _____

Sampler's Signature: _____

Witness: Name _____
Title _____

Name _____
Title _____

Sample Location: _____

Sampling Program: _____

Purpose of program: _____

Report Time Frame: _____

Sample Date: _____

Sampling Time: _____

Sampling Address: _____

Requested Analysis:
Metals: ☐
Organics: ☐
Conventional Chemistry: ☐
Micro Biological: ☐
Toxicity: ☐
Air Testing: ☐
See back of page for specifics analyses

Sample Notification:

PC: _____ Date: _____

Wet: _____ Date: _____

Micro: _____ Date: _____

Toxicity: _____ Date: _____

Metals: _____ Date: _____

Semi-Vol: _____ Date: _____

Volatile: _____ Date: _____

Current Holder Name	Signature	Title	Received Date	Received Time	Released Date

Analysis to be performed on the Sample(s):

EMD
LIMS #: _____

	Locator:	Collection Time:		Locator:	Collection Time:
-1			-6		
-2			-7		
-3			-8		
-4			-9		
-5			-10		

Sample Information: Liquid: ☐ Solid: ☐ Other: ☐ Temperature _____
Grab ☐ Composite: ☐
Start time: _____ Finish time: _____ pH _____
Container: Glass Size: _____ Color: _____ Number: ___
Plastic Size: _____ Color: _____ Number: ___ Residual Cl2 _____
Preservative ☐ Number of samples: ☐

Metals:

☐ Ag	☐ Cu	☐ Pb	☐ Other: _____	
☐ Al	☐ Fe	☐ Sb		
☐ As	☐ Hg	☐ Se		
☐ Ba	☐ K	☐ Sn		
☐ Be	☐ Mg	☐ Sr	☐ Total	
85 ☐ Ca	☐ Mn	☐ Tl	☐ Dissolved	
☐ Cd	☐ Mo	☐ V		
☐ Co	☐ Na	☐ Zn		
☐ Cr	☐ Ni			

Organics:

☐ VOC	☐ Pesticides/PCB	☐ Clopyralid	☐ Air VOC
☐ BNA	☐ Dioxin - screen	☐ Dioxin - low resolution	☐ Fixed Gases
☐ TOX	☐ Other: _____	☐ Dioxin - high resolution	☐ GC Sulfur
☐ Herbicides		☐ Tributyltin	☐ Siloxanes

Conventional Chemical:

☐ Alkalinity	☐ MBAS	☐ Solids:
☐ BOD	☐ Nitrogen:	☐ Total Solids
☐ Boron	☐ Ammonia Nitrogen	☐ Total Dissolved Solids
☐ Chloride	☐ Nitrate-N	☐ Total Suspended Solids
☐ COD	☐ Nitrite-N	☐ Settleable Solids
☐ Conductivity	☐ Organic-N	☐ Volatile Suspended Solids
☐ Cyanide (Free)	☐ Kjeldahl Nitrogen	☐ Volatile Total Solids
☐ Cyanide (Total)	☐ Oil & Grease	☐ Sulfates
☐ Flashpoint	☐ pH	☐ Sulfides, Total
☐ Fluoride	☐ Phenols	☐ Sulfides, Dissolved
☐ Grain Size	☐ Phosphate, Total	☐ Thiosulfate
☐ Hardness	☐ Phosphate, Dissolved	☐ TOC
☐ Hexavalent Chromium	☐ Radioactivity	☐ Turbidity
☐ H_2S	☐ Salinity	☐ Other:

Biological:

☐ Total Coliform	☐ Salmonella	☐ Other: _____
☐ Fecal Coliform	☐ Acute Toxicity (Fresh water)	_____
☐ E. coli	☐ Chronic Toxicity (Sea water)	
☐ Enterococcus	☐ Chronic Toxicity (Fresh water)	

Remarks: _____

APPENDIX F

Laboratory Standard Operating Procedures (City of Los Angeles)

WATER QUALITY MONITORING STANDARD OPERATING PROCEDURES

ENVIRONMENTAL MONITORING DIVISION

Hyperion Treatment Plant - Instrumental Chemistry Strategic Business Unit – Metals Laboratory

STANDARD OPERATING PROCEDURE for

INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRIC METHOD FOR TRACE ELEMENT ANALYSIS OF WATER AND WASTES

(EPA Methods 200.7)

EMD SOP# 6200.7

Effective Date:	03/01/03
Version No.:	1
Total Number of pages:	11
Prepared by:	Magdi Hanna
Pages Revised	

APPROVAL:
Laboratory Manager: Lee Huang
Signature:

Quality Assurance Manager: Jeff Beller
Signature:

TABLE OF CONTENTS

1. Scope and Application

This method may be used for the determination of dissolved, suspended, or total elements in drinking water, surface water, and domestic and industrial wastewaters. It is based primarily on EPA method 200.7, 6010B and also on SM3120. User of this SOP should be familiar with those methods and also with the EPA digestion method 30005, 3010A, 3020A, 3050B and the SM3030 series.

Dissolved elements are determined in filtered and acidified samples. Appropriate steps must be taken in all analyses to ensure that potential interferences are taken into account. This is especially true when dissolved solids exceed 1500 mg/L.

Total elements are determined after appropriate digestion procedures are performed. Since digestion techniques increase the dissolved solids content of the samples, appropriate steps must be taken to correct for potential interference effects.

Table 1 lists elements for which this method applies along with recommended wavelengths and typical estimated instrumental detection limits using conventional pneumatic nebulization. Actual working detection limits are sample dependent and as the sample matrix varies, these concentrations may also vary.

2. Summary of Method

The method describes a technique for the simultaneous multi-element determination of trace elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio-frequency (RF) inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by photosensitive device. The photocurrents from the photosensitive device are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements

3. Interferences

Several types of interference effects may contribute to inaccuracies in the determination of trace elements. They can be summarized as follows:

Spectral interferences can be categorized as (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena: and (4) background contribution from stray light from the line emission of high concentration elements. Utilizing a computer correction of the raw data, requiring the monitoring and measurement of the interfering element can compensate the first of these effects. The second effect may require selection of an alternate wavelength. The third and fourth

effects can usually be compensated by a background correction adjacent to the analyte line.

Physical interferences are generally considered to be effects associated with the sample nebulization and transport processes. Such properties as change in viscosity and surface tension can cause significant inaccuracies especially in samples, which may contain high dissolved solids and/or acid concentrations. The use of a peristaltic pump may lessen these interferences.

Molecular compound formation, ionization effects and solute vaporization effects characterize chemical Interferences. Normally these effects are not pronounced with the ICP technique, however, if observed they can be minimized by careful selection of operating conditions, by buffering of the sample, by matrix matching, and by standard addition procedures.

4. Sample Handling and Preservation

For the determination of trace elements, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents and impurities on laboratory apparatus, which the sample contacts are all sources of potential contamination. Sample containers can introduce either positive or negative errors in the measurement of trace elements by (a) contributing contaminants through leaching or surface desorption and (b) by depleting concentrations through adsorption. Thus the collection and treatment of the sample prior to analysis requires particular attention.

Before collection of the sample a decision must be made as to the type of data desired, that is dissolved, suspended or total, so that the appropriate preservation and pretreatment steps may be accomplished. Filtration, acid preservation, etc., are to be performed at the time the sample is collected or as soon as possible thereafter. If properly acid preserved (pH<2), the sample can be stored up to 6 months before analysis.

For the determination of dissolved elements the sample must be filtered through a 0.45 um pore-size membrane filter as soon as practical after collection. Acidify the filtrate with (l + l) HNO3, to a pH of 2 or less.

For the determination of suspended elements a measured volume of unpreserved Sample must be filtered through a 0.45 um pore-size membrane filter as soon as practical after collection. The filter plus suspended material should be transferred to a suitable container for storage and/or shipment. No preservative is required.

For the determination of total or total recoverable elements, the sample is acidified with (1+1) HNO3, to pH 2 or less as soon as possible, preferably at the time of collection. The sample is not filtered before processing. Following acidification, the sample should be mixed, held for sixteen hours, and then verified to be pH <2 before analysis. If pH is still high, the pH should be adjusted again, held for sixteen hours, and re-checked until verified to be pH<2 before analysis. Solid sample only require to be stored at 4^{o}C.

5. Apparatus

Inductively Coupled Plasma-Atomic Emission Spectrometer (Varian Vista-Pro)

Compaq Deskpro Personal Computer, Varian cooler/recirculator

Argon gas supply- high purity grade or better.

The ICP-AES used at EMD lab at HTP is a Varian vista-pro Analytical Instruments model Vista CCD ICP_OES. It is a simultaneous, multi-elementals analyzer with an axially viewed plasma, a purged Echelle polychromator and a solid state charged coupled device (CCD) detector with excess capacity to allow for simultaneous multi-frequencies, multi-elements analyses. It is capable of high spectral resolution even in the UV region therefore minimizing spectral interferences while increasing sensitivity of emission line detection. This SOP must be used in conjunction with the operating manual for the Varian vista-pro. The Vista-pro is computer control for plasma alignment and ignition. Its software includes the FACT (Fast Automated Curve-fitting Technique) inter-elements correction routine for spectral and background correction. This routine used spectral information of potential interfering elements, stored in its memory to synthesize a matching spectral contour adjacent to the peak of analyte of interest in the sample and subtract that from the apparent sample's spectrum to obtain the corrected spectrum. The software also contains library of all potential atomic spectral interference lines for all elements, so user can easily choose the emission line with the minimum potential for atomic spectral interference. The vista-pro is also equipped with an automatic sampler with a peristaltic pump to minimize physical interference in the sample transporting system.

6. Reagents and Standards

1. Acids used in the preparation of standards and for sample processing must be trace metals high purity grade or equivalent.

Hydrochloric acid-Conc. (sp gr 1.19)

Nitric acid-Conc. (sp gr 1.41).

2 Deionized, Distilled Water-Prepared by passing distilled water through a mixed bed of cation and anion exchange resins. Deionized, distilled water is used for the preparation of all reagents, calibration standards and as dilution water. The purity of this water must be equivalent to ASTM Type II reagent water of Specification.

3. Standard stock solutions may be purchased or prepared from ultra high purity grade chemicals. Single element stock solutions of 1000 mg/L, used here, were purchased from SPEX and from Environmental Resource Associate.

4. Mixed Calibration Standard Solutions- stock of the mixed calibration were purchased from Inorganic Ventures Inc., Ultra Scientific and from SPEX. These stocks included:

WW-IPC-1 (1000 mg/L each P, K; 200 mg/L each Al, As, Ba, Be, B, Cd, Ca, Ce, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Hg, Ni, Se, Na, Sr, Tl, V, Zn; 25 mg/L Ag)

WW-IPC-2 (1000 mg/L SiO2, 200 mg/L each Sb, Mo, Sn, Ti)

ICM-240 (100 mg/L each P, K, Si; 20 mg/L each Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Hg, Mo, Ni, Se, Na, Sr, Tl, Sn, V, Zn; 5 mg/L Ag)

ICM-245 (50 mg/L P, 25 mg/L each Al, Sb, As, Ba, B, Cr, Cu, Fe, Pb, Li, Mn, Ni, Se, Si, Sr, Tl, Zn, 10 mg/L each Cd, Co, Mn, Sn, V, 5 mg/L each Be, Hg, 2.5 mg/L Ag)

LPC Standard 1 (constituents and concentration the same as ICM-240)

LPC Standard 2 (same as ICM-245) etc.

The working mixed calibration standards were prepared by combining appropriated volumes of the stock standard solutions in volumetric flasks. The following working mixed calibration standard are used:

Std#1 (ML Be, Pb)=0.002 mg/L Be, and 0.005 mg/L Pb, from a mixture of the single stocks of Be and Pb.

Std#2 (ML 0.01)=0.01 mg/L each of Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Mo, Ni, Se, Na, Sr, Tl, Sn, V, Zn, 0.05 mg/L each of K, SiO2 and 0.00125 mg/L of Ag from a serial dilution of the mixture of equal volume of WW-IPC-1 and WW-IPC-2. Omit Ag at this low concentration in the actual calibration.

Std#3 (ML Ag)=0.08 mg/L each of Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Mo, Ni, Se, Na, Sr, Tl, Sn, V, Zn; 0.40 each of K, SiO2 and 0.01 of Ag from a serial dilution of the mixture of equal volume of WW-IPC-1 and WW-IPC-2.

Std#4 (1.0 mg/L)=1.0 mg/L each of Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Mo, Ni, Se, Na, Sr, Tl, Sn, V, Zn; 5.0 mg/L each of K, SiO2 and 0.125 mg/L of Ag from a serial dilution of the mixture of equal volume of WW-IPC-1 and WW-IPC-2.

Std#5 (4.0 mg/L)=4.0 mg/L each of Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Mo, Ni, Se, Na, Sr, Tl, Sn, V, Zn; 20 mg/L each of K, SiO2 and 0.50 mg/L of Ag from a serial dilution of the mixture of equal volume of WW-IPC-1 and WW-IPC-2.

It should be noted that if the analysis of the metal components contained in WW-IPC-2 are not required (i.e., do not need Sb, Mo, SiO2 and Sn) then only the stock of WW-IPC-1 should be used in the preparation of Std#2 to Std#5. Further more since the method requires only blank and three others calibration standards for the calibration of the instrument, the analyst has the option not to include one or two of the ML mixed calibration standards (if this exclusion still meet the ML requirements of the regional water quality control board for the permit reporting) in the actual calibration.

Std#6 (20.0 mg/L)= 20.0 mg/L each of Al, Na, Fe, K, Ca, Mg from the single stocks of 1000 mg/L of Al, Na, Fe, K and Ca.

Std#7 (40.0 mg/L)= 40.0 mg/L each of Al, Na, Fe, K, Ca, Mg from the single stocks of 1000 mg/L of Al, Na, Fe, K and Ca.

Std#6 and 7 are included here only if the analyst want to extend the upper linear dynamic range of those elements by monitoring of the lower sensitive wavelengths of those elements.

The mixed standard solutions are transferred to a polyethylene bottle for storage. Fresh mixed standards should be prepared as needed with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample.

The acceptable correlation coefficient of linearity for the calibration of each frequency must be 0.998 or greater.

5. Two types of blanks are required for the analysis. The calibration blank is used in establishing the analytical curve while the reagent blank is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

The calibration blank is prepared by diluting 10 ml of conc. HNO3 to 1000 ml with deionized, distilled water.

The reagent blank must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

6. Instrument performance check (IPC) solution is prepared by the analyst using mixture of WW-IPC-1+2. The IPC solution is used to periodically verify instrument performance or drift during analysis. It should be prepared in the same acid mixture and same source as calibration standards. Silver must be limited to<0.5 ppm while potassium and silica should be at 10 ppm. For all other analytes a concentration of 2 ppm is recommended. Analysis of the IPC solution immediately following calibration must verify that the observed values are within 5% of the expected values. Subsequent analyses of the IPC solution must be within 10% limit. Analyze the IPC solution following each 10 samples and at the end of the run. If the calibration cannot be verified within the specified limits, reanalyze either or both the IPC solution and the calibration blank. If the second analysis of the IPC solution or the calibration blank confirm calibration to be outside the limits, sample analysis must be discontinued, the cause determined, corrected and/or the instrument recalibrated. All samples following the last acceptable IPC solution must be reanalyzed.

7. Spectral interference check (SIC) solution: Prepared by the analyst, using a mixture of IPC 1+2 2.0 ppm conc. Spiked with 100 ppm of the single analytes Al, Fe, Na, K, Ca, Mg. This solution is to verify the FACT feature used to separate the interferer peaks from the interference analytes, should confirm an operative interference that is 10% range of the analyte conc.

8. The quality control sample (QCS): Must be obtained from an outside source different from the standard stock solutions used for the preparation of the calibration standards and should be prepared in the same acid matrix as the calibration standards at a concentration > or = 1 mg/L, except for silver, which must be limited to a concentration of 0.5 mg/l (in our case ICM-240 is used from ULTRA SCIENTIFIC with the proper dilution).

9. Laboratory fortified sample matrix (LFM) and its duplicate: Prepare by adding 1.0 ml of ICM240 stock into an aliquot of the sample (100 ml for surface, ground water, treatment plant effluents and 50 ml for industrial waste samples).

10. Laboratory fortified blank (LFB): Prepare by adding 1 ml of ICM240 stock into calibration blank and make up volume to 100 ml. It must be treated the same as sample in a batch (must gone thru the same sample preparation steps).

7. Safety

The toxicity and carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential

health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis.

Safety goggle and protective lab coat must be worn all the time while working in the lab. Wear glove when handle samples and chemicals.

8. Procedure

Sample Preparation: Refer to (EPA method 3005, 3010A, 3020A and SM3030) SOP on sample preparation.

Instrument start-up and warm-up procedures:

1. **Open the Argon supply, turn on the cooling system, attach the tubing in the peristaltic pump.**
2. **In the main menu of the ICP program, set "instrument parameters" to:**

   Coolant flow = 12-13 ml/min

   Auxiliary flow =1.5ml/min,

   Nebulizer flow = 0.9ml/min

4. **Turn on the pump and the hood the moment the plasma is lighted. The instrument is allowed to stabilize for at least 30 minutes before analysis is started.**
5. **Reprofile optics and optimize the torch position before actual analysis is done once a month as recommended by the manufacture.**

Sample Analysis

1. **Choose and update the method and prepare the standards and samples sequence.**
2. **Calibrate the instrument then analyze the samples.**
3. Analyze calibration blank, Instrument Performance Check , Spectral interference check at the frequency specified in the method **(**see section 11).

9. Calculation

Reagent blanks (Section 6.5) should be subtracted from all samples. This is particularly important for digested samples requiring large quantities of acids to complete the digestion.

If dilutions were performed, the appropriate factor must be applied to sample values.

Data should be rounded to the thousandth place and all results should be reported in mg/L up to three significant figures.

10. Data Management

Raw data are stored in ICP software under the filename "E:\ICP\2003\yymmdd.CSV". For data reduction, the same data are extracted and transferred to "EMDB/ICP_DATA/2003". Final results are manually entered into Laboratory Information Management System. A hard copy of all the raw data is kept in the laboratory for five years.

11. Quality Control

The initial demonstration of performance for this method consists of conducting Linear Dynamic Range (LDR), QCS, and Method Detection Limit (MDL). The first two requirements are discussed below.

Check the instrument standardization and method performance by analyzing appropriate quality control check standards as follow:

Instrument performance check standard (IPC) containing the elements of interest are analyzed immediately following a blank, after the calibration, and at a frequency of 10% thereafter. This check standard is used to determine instrument drift. If agreement is not within 5% initially and 10% subsequently of the expected values the analysis is out of control. The analysis should be terminated, the problem corrected, and the instrument recalibrated.

Laboratory reagent blank (LRB) The laboratory must analyze at least one LRB with each batch of 20 or fewer samples of the same matrix. When LRB values constitute 10% or more of the analyte level determined for a sample or is 2.2 times the analyte MDL whichever is greater, fresh aliquots of the samples must be prepared and analyzed again after the source of contamination has been corrected and acceptable LRB values have been obtained.

Spectral interference check (SIC) is analyzed at the beginning, end, and at periodic intervals throughout the sample run to verify interelement and background correction factors. Results should fall within the established control limits of one and a half times the standard deviation of the mean value. If the results are not within the control limit, the analysis is terminated, the source of the problem identified and corrected and the instrument recalibrated.

A quality control sample (QCS) obtained from an outside source must first be used for the initial verification of the calibration standards. Before any laboratory can use this method it must demonstrate that the mean concentrations from three analyses of the QCS are within 5 % of the stated values. The required frequency for the analysis of QCS is quarterly but it is this laboratory practice to analyze QSC with every batch run.

Laboratory fortified blank (LFB): The laboratory must analyze at least one LFB with each batch of samples. If 1 ml of ICM 240 is use the analytes concentrations would be as follow K=1.0, Ag=0.05 and the rest of elements= 0.2 ppm, the LFB recovery must be between 85-115% or within the statistical control limit of mean% recover +/- 3 STDEV (Standard deviation), whichever is lower. The number of the data points use to determine the STDEV are between 20 to 30 and the STDEV is updated whenever a new set of 5-10 new data points are available.

Any analyte falls outside the required control limits; source of the problem should be identified and resolved before continuing analyses.

Laboratory fortified matrix (LFM) Run matrix spike sample at a frequency of one and a duplicate per matrix batch of 10 samples. The spike concentrations should be the same as those of the LFB. The spike recovery should be within 70% to 130% of the true value. Do not calculate the percent recovery for constituent that the spike amount is lower than 30 % of it background value. The maximum relative percent different (RPD) allowed for LFM and its duplicate is 15%.

The upper limit of the linear dynamic range has to be established before this method can be used. This could be achieved by running the standard with increasing concentration against a normally run calibration set (one blank and three mixed calibration standards). The upper limits LDR are the highest concentrations for each element where recovery is equal or greater than 90% of the expected values. The upper LDR for the Varian Vista-pro ICP are list in table 1. Any samples that has its concentration exceeds 90% of the upper LDR has to be diluted and reanalyzed.

12. Lowest Reporting Level

ML and MDL for metals by EMD lab at HTP are listed in page 11 of this SOP.

13. Precision and Accuracy

The Quality Assurance Branch (QAB) of the Environmental Monitoring Systems Laboratory – Cincinnati (EMSL-CI), conducted an interlaboratory study of metal analyses by this method. Synthetic concentrates containing various levels of the twenty-five elements listed in Table 4 were added to reagent water, surface water, drinking water and three effluents. These samples were digested by either the total digestion procedure or the total recoverable procedure.

14. References

EPA Method 200.7, 1994
EPA Method 6010B, 1996
SM 3120B, Metals By Plasma Emission Spectroscopy, Standard Method for the Examination of Water and Wastewater, 18 th

15. Appendices

TABLE 1: WAVELENGTHS, INSTRUMENT DETECTION LIMITS

Analyte	Wavelength (nm)	Detection Limit (DI water) mg/l	Reporting & ML Limit mg/l	Upper LDR Limit mg/L
Aluminum	308.215	0.008	0.20	200
Antimony	206.833	0.002	0.05	20
Arsenic	193.759	0.008	0.01	20
Barium	493.409	0.0005	0.01	10
Beryllium	313.042	0.0005	0.002	10
Cadmium	226.502	0.0005	0.01	10
Calcium	315.887	0.018	0.20	50
Chromium	205.552	0.001	0.010	10
Cobalt	228.616	0.0005	0.01	10
Copper	324.754	0.001	0.01	10
Iron	259.940	0.014	0.10	10
Lead	220.353	0.002	0.005	10
Magnesium	279.078	0.008	0.20	40
Manganese	257.610	0.001	0.01	10
Molybdenum	202.032	0.001	0.01	10
Nickel	231.604	0.0005	0.02	10
Potassium	766.491	0.031	0.20	100
Selenium	196.026	0.004	0.01	20
Silver	328.068	0.0005	0.01	2.5
Sodium	589.592	0.051	1.0	120
Strontium	407.771	0.0005	0.01	10
Thallium	190.794	0.0005	0.01	10
Vanadium	292.401	0.0005	0.01	20
Zinc	213.857	0.006	0.02	10
Tin	189.927	0.006	0.01	10

a. The wavelengths listed are recommended because of their sensitivity and overall acceptability. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference.

References

EPA Method 6010B, 1998
EPA Method 200.7 Revision 4.4

ENVIRONMENTAL MONITORING DIVISION
Hyperion Treatment Plant - Instrumental Chemistry Section – Metals Laboratory
STANDARD OPERATING PROCEDURE for

INDUCTIVELY COUPLED PLASMA-MASS SPECTROSCOPY METHOD FOR TRACE ELEMENT ANALYSIS OF WATER AND WASTES

(EPA Methods 200.8, Rev. 5.4)

EMD SOP# 6200.8

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Revision by: Huyen Nguyen

APPROVAL:
Laboratory Manager: Lee Huang
Signature:

Quality Assurance Manager: Jeff Beller
Signature:

TABLE OF CONTENTS

1.0 SCOPE AND APPLICATION

This Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) method may be used for the determination of dissolved and total recoverable elements in ground water, surface water, domestic and industrial wastewaters. This SOP is based primarily on 1994 Revision 5.4 of EPA Method 200.8. User of this SOP should be familiar with EPA method 200.8 (Rev. 5.4 and Rev. 5.5), EPA method 200.2, EMD SOP # METALS 6200.8, EMD SOP # METALS 0024 and also with the Region 9 EPA SOP 507, SOP 403 and SOP 405.

To confirm approval of this method for use in compliance monitoring programs [e.g., Clean Water Act (NPDES)] consult the appropriate sections of the Code of Federal Regulation (40 CFR Part 136 Table 1B for NPDES), the latest Federal Register announcements, and the Region 9 EPA Interim Approval of Method 200.8 in October 2002.

Dissolved elements are determined after filtering with a 0.45um pore-size membrane filter and then acidifying the filtrate to match the acid matrix of the calibration standards.

With the exception of silver, samples may be analyzed directly by pneumatic nebulization without acid digestion if the sample has been properly preserved with acid and has turbidity of <1 NTU (nephelometric turbidity units) at the time of analysis. This total recoverable determination, procedure is referred to as "direct analysis".

For the determination of total recoverable elements in aqueous samples as well as in sludge and soil samples, digestion is required (EMD SOP # METALS 0024). The digestion techniques described in this SOP will dissolve almost all elements that could become “environmentally available” but would not dissolve elements, bound in silicate structures, considered as “not mobile” in the environment. Since digestion increases the dissolved solids content of the samples, appropriate steps must be taken to reduce potential interference and prevent damage to the electron multiplier detector by diluting the sample or reducing sample volume to ensure that dissolved solids do not exceed 0.2% (w/v).
Aqueous samples containing suspended or particulate material ≥ 1% (w/v) should be digested as solid sample.

The total recoverable sample digestion procedure is suitable for determination of silver concentration up to 0.1 mg/L. If aqueous samples contain higher silver concentration, smaller well mixed aliquot should be used to bring the silver concentration in analysis solution to less than 0.1 mg/L. Solid samples containing concentrations of silver > 50 mg/kg should be treated in a similar manner.

The total recoverable sample digestion procedure will solubilize and hold in solution only minimal concentration of barium in present of free sulfate, so barium analysis should be completed as soon as possible after sample digestion.

The total recoverable sample digestion procedure is not suitable for the determination of volatile organo-mercury compounds.

This method, approved for use in compliance monitoring programs [e.g. the Federal National Pollution Discharge Elimination System (NPDES)], is required by SWRCB that the lowest standard concentration in the calibration curve be equivalent to the adopted Minimal Levels (MLs) specified in table 1.
Table 1 lists elements for which this method applies with instrument detection limits (IDL), method detection limit (MDL), minimum level (ML) and upper linear dynamic range (ULDR) using Perkin Elmer Elan 9000 ICP-MS.

2.0 SUMMARY OF METHOD

An aliquot of a well-mixed, homogeneous sample is accurately weighed or measured for sample processing. For total recoverable analysis of a solid or an aqueous sample containing undissolved materials, analytes are first solubilized by gentle refluxing with nitric and hydrochloric acids. For total recoverable analysis of biosolids, analytes are solubilized by refluxing with nitric acid. Organic materials in the sample are then oxidized with hydrogen peroxide, and analytes are further solubilized by refluxing with hydrochloric acid. After cooling, the sample is made up to volume, is mixed and centrifuged or allowed to settle overnight prior to analysis. For the determination of dissolved analytes in a filtered aqueous sample aliquot, or for the "direct analysis" total recoverable determination of analytes in sample where turbidity is <1 NTU, the sample is made ready for analysis by the appropriate addition of nitric acid, and then diluted to a predetermined volume and mixed before analysis.

The method describes a technique of multi-element determination of trace elements by ICP-MS. Liquid samples are nebulized and the produced aerosol is transported to the plasma torch where desolvation, atomization and ionization occur. The resulting ions (primarily singly charged positive ions) are then extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a quadrupole mass spectrometer. The ions transmitted through the quadrupole are then detected with a dynode electron multiplier detector and the ion information processed by a data handling system, which takes into account of polyatomic ions interferences and isobaric elemental interferences. Internal standards are used to compensate for instrumental drift and erroneous signal enhancement or suppression caused by sample matrix.

3.0 INTERFERENCES

Several types of interference effects may contribute to inaccuracies in the determination of trace elements by ICP-MS. They include mass spectral interferences and physical interferences. Mass spectral interferences can be categorized as isobaric elemental interferences, isobaric polyatomic ion interferences, and abundance sensitivity.

Isobaric Elemental Interferences occur when isotopes of different elements form singly or doubly charged ions which have the same nominal mass-to-charge ratio and which cannot be resolved (i.e. separated) by the mass spectrometer. However, most elements determined by this method have at least one isotope that is free of isobaric elemental interference. Of the analytical isotopes used in the method only molybdenum-98 (ruthenium-98) and selenium-82 (krypton-82), antimony-123 (technetium-123) have isobaric elemental interference. For isotopes that must be monitored, only cadmium-114 and indium-115 have isobaric interference from tin. Correction of data for these isotopes are made by measuring the signal from another isotope of the interfering element and using its natural abundance ratio to calculate the intensity to be subtracted from the signal of the isotope of interest. Usage of high purity krypton-free argon will greatly reduce the effect of krypton-82 on selenium-82 analysis.

Isobaric Polyatomic Ion Interferences: These are caused by molecular ions that have the same nominal mass-to-charge ratio as the isotope of interest and which cannot be resolved by the mass spectrometer. Most of these ions have been identified; they are commonly formed in the plasma or interface system from support gases or sample components. These interferences must be recognized, and corrections to the data must be performed. The equations for these corrections need to be established at the time of analysis, since they are dependent on sample matrix and instrument operating conditions. The presence of chloride in sample results in the formation of singly charged ions $^{40}Ar^{35}Cl$, $^{35}Cl^{16}O$, $^{37}Cl^{16}O$ that interfere respectively with ^{75}As, ^{51}V, and ^{53}Cr. Although correction the for interference of $^{40}Ar^{35}Cl$ on the analytical isotope ^{75}As can be made using the signal for $^{40}Ar^{37}Cl$ and the correction for $^{35}Cl^{16}O$ on the isotope ^{51}V can be performed using the signal for $^{37}Cl^{16}O$, no correction can be made for the interference of $^{37}Cl^{16}O$ on the monitored isotope ^{53}Cr. Interference of $^{95}Mo^{16}O$ on the monitored isotope ^{111}Cd can be corrected using the signal for $^{92}Mo^{16}O$. The presence of bromide in sample can result in the formation of $^{81}Br^{1}H$ that will elevate recovery for Se at mass 82. If this correction is required then bromine at mass 79 and 81 need to be added to this method and monitored.

Abundance Sensitivity is defined as the degree to which the wings of a large ion peak contribute to an adjacent ion peak. The abundance sensitivity is affected by ion energy and quadrupole operating pressure. The spectrometer resolution should be adjusted to minimize these interferences.

Physical interferences are generally associated with the sample transport into the plasma, sample conversion processes in the plasma, and transmission of ions from the plasma through the interface into the mass spectrometer. Physical interferences may occur in the transfer of solution to the nebulizer (e.g., viscosity effects), in the process of aerosol formation and transport into the plasma (e.g., surface tension effects), and during excitation and ionization processes in the plasma. Such differences in viscosity and surface tension between samples and standards can cause significant inaccuracies especially if samples contain high dissolved solids. Internal standardizations are used to compensate for these physical interferences. High levels of dissolved solids in the sample may contribute deposits of material on the sampler cone and the skimmer cone reducing

the effective diameter of the orifices and therefore the ion transmission. Samples should be diluted if dissolved solids levels exceed 0.2% (W/V).

Memory interferences result when isotopes of elements in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the sampler and skimmer cones, and from the buildup of sample material in the plasma torch and spray chamber. The possibility of memory interference should be recognized within an analytical run and suitable rinse times should be used to reduce them. Memory interferences may be assessed within an analytical run by looking at the values of the three replicates. If the integrated signal values drop consecutively, the analyst should examine the analyte concentration in the previous sample to identify the possibility of a memory effect. If previous sample has high concentration, the sample should be reanalyzed after a long rinse period. In the determination of mercury, gold at 100 ppb is to be added to rinse solution to minimize memory effect.

4.0. SAMPLE COLLECTION, PRESERVATION AND PREPARATION

4.1. Prior to the collection of an aqueous sample, consideration should be taken to the type of data desired (i.e. dissolved, total or total recoverable) so that appropriate preservation and pretreatment steps can be taken. The pH of all aqueous samples must be tested immediately prior to aliquoting for processing or "direct analysis" to ensure that the sample has been properly preserved. If properly acid preserved, the sample can be held up to 6 months.

4.2. For the determination of dissolved elements, the sample must be filtered through a 0.45 μm pore-size membrane filter as soon as practically possible after collection. Acidify the filtrate immediately following filtration with (l + l) HNO_3, to a pH of 2 or lower.

4.3. For the determination of total recoverable elements, the samples are not filtered but acidified with (1+1) HNO_3, to pH 2 or less as soon as possible. Following acidification, the sample should be mixed, held for sixteen hours, and then verified to be pH < 2 just prior to withdrawing an aliquot for analysis. If for some reason the pH is verified to be higher than 2, more acid must be added and the sample held for sixteen hours until verified to be pH < 2.

4.4. Aqueous samples containing suspended or particulate material > 1% (w/v) should be extracted as a solid type sample.

4.5. Sample preparations for dissolved elements are suitable filtration through a 0.45 μm pore diameter membrane filter, acid preservation and then dilution to a predetermined volume. Analytes may be analyzed directly without acid digestion of samples. Silver is only slightly soluble in the presence of chloride unless there is a sufficient chloride concentration to form soluble chloride complex. Therefore hydrochloric acid should be added to filtered samples to keep silver in solution (1 mL of HCl to 50 mL of sample) and analysis should be completed as soon as

possible after sample preparation. If low recoveries of silver occur in fortified sample matrices, it is recommended that samples be digested prior to the determination of silver. In order to reduce potential interferences, dissolved solids should not exceed 0.2% (w/v).

Sample preparation for total recoverable analytes must include a digestion/extraction step (EMD SOP # METALS 0024).

5.0 APPARATUS

5.1. Inductively Coupled Plasma-Mass Spectrometer (Perkin Elmer SCIEX ELAN 9000).

5.2. Dell Optiplex Personal Computer Hardware/ Perkin Elmer ELAN Data Station-Instrument Control Software Version 2.4 1994-2001

5.3. Perkin Elmer AS-93plus Auto-sampler

5.4. PolyScience Recirculator/Chiller Model Number 3370

5.5. Either liquid or gaseous argon, purity 99.996%, oxygen < 5 ppm, hydrogen <1 ppm, nitrogen <20 ppm, water < 4 ppm.

6.0 REAGENTS AND STANDARDS

6.1 Concentrated acids used in the preparation of standards and for sample processing must be ultra-high purity grade or equivalent (Fisher Scientific – Optima grade, J.T. Baker - Ultrex grade.)

Hydrochloric acid-concentrated (sp. gr. 1.19)
Nitric acid-concentrated (sp. gr. 1.41).

6.2 Deionized water, used in the preparation of all reagents and obtainable from the central water purification system of the Pregerson Laboratory Building, is prepared by passing potable water through a mixed bed of cation and anion exchange resins, and has purity equivalent to ASTM Type I grade water.

6.2 1:1 (vol/vol) nitric acid prepared by adding 25 ml concentrated nitric acid to 25 ml reagent water in a clean 50 ml vial.

6.3 Tuning solution 10 ppb of Mg, Rh, In, Ba, Ce, Pb, U.
The tuning solution may be purchased from Perkin Elmer or prepared from 1000 ppm single element stock solutions.

6.4 Internal Standard Stock Solutions
Solution 1: 10 ppm Bi, Ho, In, Li6 (95 % enriched) Sc, Tb, Y in 1% nitric acid.
Solution 2: 50 ppm Ge, 10 ppm Rh. in 1% nitric acid.

The Internal Standard Stock solutions may be purchased or prepared from 1000 ppm single element stock solutions.

6.5 Internal Standard Working Solution. (400 ppb Bi, Ho, In, Li6 (95 % enriched) Sc, Tb, Y; 1000 ppb Rh; 5000ppb Ge in 1% nitric acid).
Prepare by pipetting :
1.00 ml HNO3 1/1,
2.00 ml Internal Standard Stock Solution 1,
5.00 ml Internal Standard Stock Solution 2,
and dilute to 50 ml with reagent water.

6.6 Auto-lens solution. 10 ppb Be, Co, In, U.
The Auto-lens solution may be purchased or prepared from 1000 ppm single element stock solutions.

6.7 Standard Stock Solutions
ML Stock Solution 1: 20 ppm As, Se; 10 ppm Tl, Ni, Zn; 5 ppm Sb, Be, Cr, Cu, Pb; 2.5 ppm Cd, Ag.
Prepare from 1000 ppm single element stock solutions.

1 ppm Stock Solution (IPC 1+2 1ppm): 1 ppm As, Ba, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, Sr, Tl, V, Zn, Sb, Mo, Sn; 0.125 ppm Ag. Prepare by pipetting 2.0 ml HNO_3 1/1, 0.50 mL IPC-1(Inorganic Ventures, Inc), 0.50 mL IPC-2 (Inorganic Ventures, Inc) and diluting to 100 mL with reagent water.

Calibration Standards.

Prepare fresh calibration standards daily. Four standards and one calibration blank are used for the calibration of the instrument.

Calibration Blank.

Fill a 50 mL vial with approximately 20 mL of reagent water. Pipette 1 mL of 1/1 HNO3, 1.0 mL of Internal Working Solution and dilute to 50 mL with reagent water.

Calibration Standard 1 (ML):

2 ppb As, Se; 1 ppb Tl, Ni, Zn; 0.5 ppb Sb, Be, Cr, Cu, Pb; 0.25 ppb Cd, Ag.

Prepare a ML Stock Solution 2 by pipetting 2 mL HNO3 1/1, 1.0 mL of the ML Stock Solution 1 (20 ppm As, Se; 10 ppm Tl, Ni, Zn; 5 ppm Sb, Be, Cr, Cu, Pb; 2.5 ppm Cd, Ag) and diluting to 100 ml with reagent water.

Fill a 50mL vial with approximately 20 mL of reagent water, add 1 mL HNO_3, 0.50 mL of the ML Stock Solution 2, 1.0 mL of the Internal Working Solution and dilute to 50 mL with reagent water.

Calibration Standard 2:

10 ppb As, Ba, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, Sr, Tl, V, Zn, Sb, Mo, Sn; 1.25 ppb Ag.

Fill a 50 mL vial with approximately 20 mL of reagent water, add 1 mL HNO_3, 0.50 mL of the 1 ppm Stock Solution (IPC 1+2), 1.0 mL of the Internal Working Solution and dilute to 50 mL with reagent water.

Calibration Standard 3:

20 ppb As, Ba, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, Sr, Tl, V, Zn, Sb, Mo, Sn; 2.50 ppb Ag.

Fill a 50 mL vial with approximately 20 Ml of reagent water, add 1 mL HNO_3, 1.0 mL of the 1 ppm Stock Solution (IPC 1+2), 1.0 mL of the Internal Working Solution and dilute to 50 mL with reagent water.

Calibration Standard 4:

100 ppb As, Ba, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, Sr, Tl, V, Zn, Sb, Mo, Sn; 12.5 ppb Ag.

Fill a 50 mL vial with approximately 20 mL of reagent water, add 1 mL HNO_3, 5.0 mL of the 1 ppm Stock Solution (IPC 1+2), 1.0 mL of the Internal Working Solution and dilute to 50 mL with reagent water.

The acceptable correlation coefficient of linearity for each calibration is 0.998 or greater.

6.8 . Quality Control Sample (To verify calibration standards).

Quality Control Stock Solution (ICM 240):
1 ppm As, Ba, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, Sr, Tl, V, Zn, Sb, Mo, Sn; 0.250 ppm Ag.

Prepare by pipetting 2 mL HNO_3 1/1, 5.0 mL of ICM-240 (Ultra Scientific) and diluting to 100 mL with reagent water.

Quality Control Working Solution (ICM 240):

20 ppb As, Ba, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, Sr, Tl, V, Zn, Sb, Mo, Sn; 5.00 ppb Ag.

Prepare by pipetting 1 mL HNO_3 1/1, 1.0 mL of the Quality Control Stock Solution, 1.0 mL of the Internal Working Solution and diluting to 50 mL with reagent water.

6.9 Analog Stage Detector Optimization Solution.

Prepare 100 ppb Mg solution in 1% HNO_3 by pipetting 1 mL HNO_3 1/1 and 0.005 mL of 1000 ppm Mg into a 50 mL vial and dilute to 50 mL with DI water.

6.10 Dual Detector Cross Calibration Solution:

200 ppb As, Ba, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Sr, Tl, V, Zn, Sb, Mo, Sn; 25 ppb Ag.; 8 ppb Bi, Ho, In, Li6 (95 % enriched) Sc, Tb, Y; 20 ppb Rh; 100 ppb Ge; 4 ppm Se in 1% nitric acid.

Prepare by filling a 50 mL vial with approximately 20 mL of DI water, and adding 1 mL HNO_3 1/1, 5 mL of the IPC 1+2 Stock Solution (2ppm), 0.20 mL of 1000 ppm Se, 1 mL of the Internal Standard Working Solution and dilute to 50 mL with DI water.

7.0 SAFETY

The toxicity and carcinogenicity of each reagent used in this method have not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Wear glove when handle samples and chemicals.

Never view the ICP torch directly without protective eyewear. Potentially hazardous ultraviolet radiation may be emitted. Safety glasses will in general provide sufficient protection.

ICP-MS instrument generates high amounts of radio frequency energy in the RF power supply and torch box, which is potentially hazardous if allowed to escape. Safety devices and screening interlocks should not be bypassed or disconnected.

The power supply for the operation of ICP-MS is capable of generating potentially lethal voltages. No maintenance should be performed when the power is on.

Ensure that the exhaust system is working properly. The Elan 9000 ICP-MS requires two vents, one for the ICP power supply/roughing pump exhaust and another vent for the torch box exhaust. Exhaust venting is important not only to remove heat produced by the ICP torch, RF power supply and pump motors, but also to protect laboratory personnel from toxic vapors that may be produced by ICP.

Gas cylinders must be clearly marked to identify the status (e.g. full, empty, etc…), carefully secured and stored away from heat. Since cylinders have pressure-relief device that might release argon, room ventilation should be adequate to prevent accumulation of non-life-sustaining gas.

8.0 PROCEDURE

8.1 Check the following before startup:
Water chiller
Exhaust system
Vacuum roughing pumps
Cold vacuum(should be in 10^{-6} torr range). Record pressure reading in log-book.
Argon tank
Sample introduction system (pump tubing, nebulizer, spray chamber, torch, cone, etc…)

8.2 Initiate the plasma and allow a warm-up for at least 30 minutes. The tuning procedures may be carried out during warm up. Check out the following during warm-up:
Operating vacuum. Record value in log-book.
Nebulizer gas flow rate
Sample uptake rate
Spray chamber drainage

8.3 Open the EMD-Daily performance workspace and open the EMD-Daily method
Aspirate the 10 ppb tuning solution.
Click on the Analyze button in manual sample window.
Check that the RSDs for five replicates for all Be, Mg, Co, In, Rh and Pb are less than 5%.
Check that the background at mass 220 is < 30 cps.
Check that % oxides < 3%.
Check that % double charge <3%.
Mg Intensity > 100,000 cps (140,000 cps, normally)
Rh Intensity > 400,000 cps (600,000 cps).
In Intensity > 400,000 cps (700,000 cps)
Pb Intensity > 300,000 cps (450,000 cps).
If the instrument performance check passes, go to 8.11 and proceed with the samples.

8.4 If the instrument performance check does not pass, open the EMD- X-Y workspace and the EMD-X-Y method, open the real-time window by clicking on realtime icon, aspire the tuning solution and make X-Y adjustment for maximum Rh intensity. This procedure is only necessary when cones or torch have been changed.

8.5 Open the Neb-power-Lens-Oxide workspace and the EMD-Optimize method, set the RF power to 1000-1100 watts for clean water, 1200-1400 watts for soil and sediments digests and optimize the following parameters using the tuning solution:
Optimize the nebulizer argon flow.
Optimize the static lens voltage (optional).
Save the optimization file.

8.6 Open the EMD-Auto-Lens-Calibration workspace and the EMD-Autolens Calib method and perform auto-lens calibration using the Auto-lens Solution as the following:
Clear the old calibration.
Click on Get Analytes.
Click on Calibrate.
Save the optimization file, print the current settings in the default.dac using <File><Print> option and the Optimization.rop.
Go to 3 and perform Daily Performance Check.

8.7 Perform a Pulse Stage Detector Optimization.
Open the EMD Pulse Stage Optimization workspace and the EMD Optimize method.
Optimize Pulse Mode Voltage using Tuning Solution as follows:
Aspire the tuning solution.
Click on Pulse Stage Voltage tab.
Click on Get Analyte List, check that Rh appears in the Analyte field.
Select the start and end values of the potential set points at 900 and 1000 respectively and set the step value at 25.
Select Intensity Change Percent at 15% as optimization criteria.
Click on Optimize tab.
Save the Optimization file.
In the interactive window, a plot of pulse intensity vs. pulse stage voltage is displayed. The optimum point is indicated by a diamond symbol. Check that the software selected the correct point. Do not operate the detector at voltages far beyond the saturation point as this can reduce detector lifetime, cause signal drift and increase noise level.
This procedure is only required when a new detector is installed or detector voltages need to be optimized for higher sensitivity.

8.8 Analog Stage Detector Optimization.

Analog Stage Detector must be performed before performing Dual Detector Calibration. Pulse stage optimization must be performed before and after an analog stage optimization.
Open the EMD Analog Stage Optimize workspace and the EMD Analog Stage Optimization method.
Chose Analog Stage Voltage in the parameter Description box.
Click on Get Analyte List, make sure that Mg appears in the Analyte List.
Select Auto and Full in the Optimization Criteria group. Type in 12500 for the Target Gain or select Use Nmax and type in 1e9 for the target Nmax.
Aspire 100 ppb Mg solution then click on Optimize.
If the optimization is successful, a message appears starting that the optimization is complete. Save the optimization file.

8.9 Dual detector crossed calibration. Dual detector calibration is used to extend the dynamic range of the detector by normalizing the analog stage of the detector to the pulse stage. This procedure is required whenever the analyte concentrations that are needed exceed the linear dynamic range of the pulse counting.
Optimize Pulse Stage detector voltage, Analog Mode Voltage and again Pulse Stage detector voltage.
Open the EMD Dual Detector Calibration workspace. Select the EMD Dual Detector Calibration method. Check to make sure that the method contains all elements you want and there are no interference equations in the method.
If analytes are already listed on the Dual Detector Calibration page, click on Clear Calibration and then on Get Analyte List.
Enter the Start Value (-1 to -3), the End Value (8 to 12) and the step value (0.25 to 0.5) in the Lens Voltage group.
Aspire the Dual Detector Cross Calibration Solution.
Click on Calibrate tab.
The ELAN will perform 2 separate acquisitions:
The first acquisition is used as the calibration blank (lens voltage is set for zero ion transmission) and the dataset name is label Dual Calibration Blank.
The second acquisition is the actual dual calibration.
One can view the analysis progress in the real time window in Signal or Numeric Mode.
In the Interactive window, one can view the cross calibration curves for 1 to 5 isotopes plus the Pulse/Analog Gain Interpolation curve. The correlation coefficients for individual isotopes are normally at least 0.9995.
Save the optimization file.

8.10 Tuning (Mass Calibration. & Resolution)
Tuning of the Elan 9000 should be performed monthly and whenever there are changes to the ELAN's electronics or if there are needs to modify resolution for one or more elements.
Open the EMD Tuning workspace.
Open the EMD-tuning method.
Aspire the tuning solution.

Click on Tuning icon to display the Tuning window, make sure the tuning file has all the required elements in the method (He, Mg, Rh, Pb, U, Ce) and that the Measure Peak Width Only parameter is toggled Off.
Click on the Tune Mass Spec button in the tuning window to perform a full Autotune, adjusting both the mass calibration and the resolution.
Click on the Interactive icon to display the spectra of all tuning analytes.
Save the Tuning file.
Print the results of mass calibration and resolution adjustment using the Tuning.rop report format.
Check that the measured mass values remain within 0.05% of the actual mass and peak widths are approximately 0.70 amu.
In selected instances, it may be desirable to use resolution settings that are different from the default 0.7 amu. Click in the Resolution DAC value cell for the analyte you want to adjust, increase the DAC value to increase resolution (narrower the peak) or set the DAC to a smaller value to decrease the peak resolution (broaden the peak). Aspire the tuning solution and click on Tune Mass Spec to perform a full Auto-Tune.

8.11Quantitative Analysis.

Open the EMD Quantitative Analysis workspace.
Click on method icon and open the 200.8EMD method.
Enter report file name in the Report page of the method.
Click on the green R icon to view files currently in use and chose Load Dataset to select an existing dataset for the month (Feb03 for the month of February 2003 for example) or New Dataset to create a new dataset.
Prepare blank, calibration standards and load them into the auto-sampler positions 1-5 (position 1 for calibration blank; position 2 for standard 1, ML; position 3 for standard 2, 10 ppb; position 4 for standard 3, 20 ppb; position 5 for standard 5,100 ppb).
Prepare the quality control sample ICM-240, 20 ppb and load it into position 6.
Edit the Sample window and enter sample information in the batch sample page (sample name, LIMS ID, dilution factor). The frequency of QC solution analyses (e.g. calibration blank, instrument performance check solution, quality control sample, etc…) is already set in the method, so there is no need to enter QC information in sample window.
The measurement action for the first sample must be “analyze blank, standards, and samples”. Measurement action for all other samples is “ analyze sample”. Enter appropriate pump speeds for all samples. Save sample file and reopen the sample file (this must be done for the batch QC to run properly).
Prepare sample by filling a 50 mL vial with approximately 10 mL of reagent water, add 1 mL HNO_3, 1.0 mL of the Internal Working Solution, add an exact volume of digested sample (2.5 mL for 1:20 dilution or 5 mL for 1:10 dilution) and dilute to 50 mL with reagent water. Final volume is not critical since internal standards are used, so accuracy of the markings on the side of each vial is sufficient.

Load the samples into the auto-sampler positions specified in the sample file. Select the samples to be analyzed by highlighting the row number with the mouse and start the analysis by clicking on "Analyze Batch".

9.0. CALCULATION

Elemental equations for corrections of masses interference are:

Element	Mass in amu	Corrections
Vanadium	50.944	$-3.127(^{37}Cl^{16}O - (0.113 \times {}^{52}Cr))$
Arsenic	74.922	$-3.127(^{40}Ar^{37}Cl - (0.873 \times {}^{82}Se))$
Selenium	81.917	$-1.008696 \times {}^{83}Kr$
Molybdenum	97.906	$-0.110588 \times {}^{101}Ru$
Cadmium	110.904	$-1.073(^{92}Mo^{16}O - (0.712 \times {}^{106}Pd))$
Cadmium	113.904	$-0.026826 \times {}^{118}Sn$
Indium	114.904	$-0.014032 \times {}^{118}Sn$
Antimony	122.904	$-0.127189 \times {}^{125}Te$
Lead	207.977	$+ {}^{206}Pb + {}^{207}Pb$

Data should be calculated by application of internal standardization.

Reagent blank should be subtracted from all samples. This is particularly important for digested samples requiring large quantities of acids to complete the digestion.

If dilutions were performed, the appropriate factor must be applied to sample values.

Sample data should be reported in unit of µg/l for aqueous samples or mg/kg dry weight for solid samples. Do not report element concentrations below the determined MDL. For data values less than ten, two significant figures should be use for reporting element concentrations. For data values equal or greater than ten, three significant figures should be used.

The isotopes recommended for analytical determination are:

^{9}Be, ^{51}V, ^{52}Cr, ^{55}Mn, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{75}As, ^{82}Se, ^{117}Sn, ^{98}Mo, ^{107}Ag, ^{111}Cd, ^{123}Sb, ^{137}Ba, ^{205}Tl, ^{206}Pb, ^{207}Pb, ^{208}Pb.

If an element has more than one monitored isotope, examination of the concentration calculated for each isotope, or the isotope ratios, will provide useful information for the analyst in detecting a possible spectral interference. Consideration should therefore be given to both primary and secondary isotopes in the evaluation of the element concentration. In some cases, secondary isotopes may be less sensitive or more prone to

interference than the primary recommended isotopes, therefore differences between the results do not necessarily indicate a problem with data calculated for the primary isotopes.

The QC data obtained during the analysis provide an indication of the quality of the sample data and should be provided with the sample results.

10.0. DATA MANAGEMENT

The metals lab uses method 200.8 for the determination of Ag, Pb, Sb and Tl in the monthly and weekly treatment plants effluent samples. Raw data are stored by ICP-MS software under the filename "c:\elandata\reportoutput\yyyymmdd". For data reduction, the same data are transferred to "EMDB\ICP-MS\2004" using the Excel Template, developed for the metals lab, and the processed data stored in "EMDB\ICPMS_DATA\2004. Manipulation for the final concentrations and for displayed QC data could be performed thru the master sheet on the excel file. The printout data are kept in a three ring binder folder as permanent record. Final results are reported in Laboratory Information Management System.

11.0. QUALITY CONTROL

11.1 Initial Demonstration of Laboratory Performance. The initial demonstration of performance is used to characterize instrument performance and laboratory performance prior to analyses conducted by this method.

11.1.1 Linear Calibration Range.

Linear Calibration Range should be determined before using the ICP-MS for producing any legal reporting data, and whenever there are changes in the detector voltages, RF generator, sample introduction system (change in nebulizer or spray chamber type).

Calibrate the instrument as usual, and run a series of increasing concentration standards. The upper linear dynamic range (ULDR) limit is defined as the concentration where the measured value is within 10% of the actual prepared value of the standards. Care should be taken to avoid potential damage to the detector during this process. ULDR are listed in table 1. When analyze sample that has concentrations of any element greater than 90 % of the ULDR that sample must be diluted and reanalyzed.

11.1.2 Quality Control Sample.

On a quarterly basis, to verify the calibration standards and acceptable instrument performance, it is required to analyze a Quality Control Sample (QCS). The determined mean concentration from 3 analyses of the QCS must be within 10%

of the stated QCS value. If the QCS is not within the required limits, an immediate second analysis of the QCS is recommended to confirm unacceptable performance. If the second analysis is unacceptable, problem must be identified and corrected.

11.1.3 Instrument Detection Limits (IDLs)

IDL should be determined whenever there is any significant change to the instrument. Calibrate the instrument. Run a blank as if it were a sample for a series of 10 sequential measurements with rinsing in between each measurement. Calculate the standard deviation and multiply by 3 to obtain the IDL. IDL are listed in table 1.

11.1.4 Method Detection Limits (MDL)

MDL should be established for all analytes using reagent water fortified at a concentration of two to five times the estimated detection limit. Analyze seven replicate aliquots of the fortified reagent water that have been processed through the entire analytical method and calculate the MDL as follows:

MDL = t x (Standard Deviation of the replicate)

Where t is the Student's value for a 99% confidence level with n-1 degrees of freedom (t = 3.14 for seven replicate). MDL are listed in table 1. The determination of MDL in reagent water represents a best-case situation and does not reflect possible matrix effects of real samples. The MDLs must be sufficiently low to be able to detect analytes at the required levels according to compliance monitoring regulation. MDLs should be determined annually or whenever there is a change in instrument operating conditions.

11.2. Mandatory Laboratory Performance Quality Assurance Procedures

11.2.1. Laboratory Reagent Blank (LRB)

Laboratory Reagent Blank (LRB) is an aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The LRB is used to determine if analytes or other interferences are present in the laboratory environment, reagents, or apparatus. A minimum of one LRB must be run with each batch of 20 samples of the same matrix. LRB values greater than the MDL indicate laboratory or reagent contamination. The values of LRB and their standard deviations must be kept on file and be available for review.
The upper control limit for LRB can be developed when a minimum of 20 data become available as follows:

Upper Control Limit = x + 1.5 S

Where x is the mean of LRB and S is the standard deviation of the mean LRB.
For NPDES test program, whenever LRB values constitute 10% or more of the analyte level determined for the sample or is 2.2 times the analyte MDL, whichever is greater, fresh aliquots of the samples must be prepared and analyzed again for the affected analytes after the source of contamination has been corrected and acceptable LRB values have been obtained.

11.2.1. Laboratory Fortified Blank (LFB)

Laboratory Fortified Blank is an aliquot of reagent water to which known quantities of the analytes are added. The LFB is treated and analyzed exactly like a sample. The purpose of analyzing LFB is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

The laboratory must analyze at least one LFB with each batch of samples. Calculate accuracy as percent recovery using the following equation

$$Rec. = (LFB - LRB) / S \times 100$$

Where: Rec. = Percent Recovery
LFB = Lab. Fortified Blank Result
LRB = Lab. Reagent Blank Result
S = Concentration of analyte added to fortify the LRB

The percent recovery for the LFB should be within the required control limits of 85% - 115%. If the recovery is not in control, the source of the problem should be identified and resolved before analysis is continued. The percent recoveries of LFB and their standard deviations must be kept on file and be available for review.

Optional upper and lower control limits can be developed when a minimum of 20 performance data become available as follows:

$$\text{Upper Control Limit} = x + 3S$$
$$\text{Lower Control Limit} = x - 3S$$

Where x is the mean percent recovery of LFB and S is the standard deviation of the mean percent recovery.

The optional control limits must be equal to or better than the required control limits of 85% - 115%. After each five new recovery measurements, new control limits are calculated using the most recent 20 data points. For simplification and due to the rather low number of batches run by this lab, annual updating of ongoing control limits is accepted.

11.2.2. Instrument performance check (IPC)

For all determinations the laboratory must check instrument performance and verify that the instrument is properly calibrated on a continuing basis. To verify calibration, run the calibration blank and calibration standards (10 ppb or 20 ppb) as surrogate samples immediately following each calibration routine, after every ten samples and at the end of the sample run. The analysis of all analytes within the standard solutions must be within 10% of the calibration. If the calibration cannot be verified within the specified limits, the instrument must be re-calibrated. If the continuing calibration check is not confirmed within 15%, the previous ten samples must be re-analyzed after recalibration. If the sample matrix is responsible for the calibration drift, the previous 10 samples should be reanalyzed in groups of five between calibration checks to prevent a similar drift situation from occurring.

11.3. Assessing Analyte Recovery and Data Quality

11.3.1 Laboratory Fortified Sample Matrix (LFM).

Sample homogeneity and the chemical nature of the sample matrix can affect analyte recovery and the quality of data. LFM procedure is required to assess these effects. Known amounts of analytes are added to a minimum of 10% of the samples. In each case the LFM aliquot must be a duplicate of the aliquot used for sample analysis and analytes added prior to sample preparation. For water samples, the added analyte concentration must be the same as that used in the laboratory fortified blank or 1-5 times the background concentration, whichever is greater. Percent recovery for each analyte, corrected for background concentration, is calculated using the following formula:

$$R = (C_s - C) \times 100 / S$$

Where R = percent recovery
C = sample background concentration
C_s = fortified sample concentration
S = concentration of analyte added to fortify the sample

The LFM range is 70% - 130%. Recovery calculations are not required if the concentration of the analyte added is less than 30% of the sample background concentration.
Optional upper and lower control limits can be developed when a minimum of 20 performance data become available as follows:

Upper Control Limit = x + 3 S
Lower Control Limit = x - 3 S

Where x is the mean percent recovery of LFM and S is the standard deviation of the mean percent recovery. The optional control limits must be equal to or better than the required control limits of 70% - 130%. After each five new recovery measurements, new control limits are calculated using the most recent 20 data points.

If the recovery falls outside the designated range and laboratory performance is shown to be in control (Sect. 11.2), the recovery problem encountered with the fortified sample is judged to be matrix related, not system related. The data user should be informed that the result for the unfortified sample is suspect, due to either the heterogeneous nature of the sample or an uncorrected matrix effect.

11.3.2. Internal Standard Responses.

The analyst is expected to monitor the responses from the internal standards throughout the sample set being analyzed. Ratios of the internal standards responses against each other should also be monitored routinely. This information may be used to detect potential problems caused by mass dependent drift, errors incurred in adding the internal standards or increased in the concentrations of individual standards caused by background contributions from the sample. The absolute response of any one internal standard must not deviate more than 60% - 125% of the original response in the calibration blank. If greater deviations are observed, flush the instrument with the rinse blank and monitor the responses in the calibration blank. If the responses of the internal standards are now within the limit, take a fresh aliquot of the sample, dilute by a further factor of two, add the internal standards and reanalyze. If after flushing the response of the internal standards in the calibration blank are out of limits, terminate the analysis and determine the cause of the drift. Possible cause of drift may be a partially blocked sampling cone or a change in the tuning condition of the instrument.

12.0 REPORTING LEVEL

A reporting level is the lowest concentration of a detected substance that must be reported for specific regulatory purposes, such as determining compliance with effluent limitations and water quality criteria or objective.

The reporting limit (RL) is obtained by first determining the MDLs. A multiple of MDL level is spiked into reagent water and processed as a sample. If the spike is recovered within 60% and 140%, the test concentration is the lowest RL. The RL for most elements is about five times the MDL and represents a practical and routinely achievable detection limit with a relatively good certainty that any reported value is reliable. If a sample is diluted prior to analysis, the RL is multiplied by the dilution factor.

For NPDES permit testing, the metals lab uses “Minimum Level (ML)” as RL. ML is the concentration in a sample that is equivalent to the concentration of the lowest calibration

standard analyzed according to the method. The ML and MDL for this method are listed in [EMD_INFO.METALS. 2003-MDL] 62008.XLS file.

13.0. PRECISION AND ACCURACY

13.1. Precision.

Check that the relative standard deviations of three replicates (Replicate RSD) are less than 5% for standards and samples.

13.2. Accuracy.

To verify the calibration standards, it is recommended to run QCS (ICM-240) at the beginning and at the end of the run. The analysis of a QCS prepared to a concentration of 20 ppb (5 ppb for Ag) must be within 90%-110% of the stated value initially and within 15% at the end. All requirements for laboratory reagent blank (LRB), laboratory fortified blank (LFB), laboratory fortified matrix (LFM) must be satisfied before using the data for reporting.

14.0. REFERENCES

14.1. EPA Method 200.8 Revision 5.4, May 1994, "Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma-Mass Spectrometry".

14.2. EPA Method 200.8 Revision 5.5 "Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma-Mass Spectrometry".

14.3. EPA Method 200.8 Using the ELAN 6000/6100 ICP-MS PerkinElmer Spectrometry

14.4. ELAN ICP-MS Hardware Manual, 1995, PerkinELmer.

14.5 Region 9 EPA SOP 507, November 2002

14.6 Region 9 EPA SOP 403, November 2002

14.7 Region 9 EPA SOP 405, November 2002

15.0 APPENDIX

Element	Isotope	ML in ppb	IDL in ppb	MDL in ppb	ULDR in ppb
Be	^{9}Be	0.5	0.01	0.02	30
V	^{51}V	1.0	0.02	0.02	200
Cr	^{52}Cr	0.5	0.04	0.06	200
Cr	^{53}Cr	0.5	0.03	0.05	200
Mn	^{55}Mn	1.0	0.009	0.08	200
Co	^{59}Co	1.0	0.01	0.005	200
Ni	^{60}Ni	1.0	0.01	0.07	200
Cu	^{63}Cu	0.5	0.009	0.1	200
Cu	^{65}Cu	0.5	0.009	0.1	200
Zn	^{66}Zn	1.0	0.02	0.1	200
Zn	^{67}Zn	1.0	0.04	0.2	200
Zn	^{68}Zn	1.0	0.04	0.1	200
As	^{75}As	2.0	0.04	0.4	200
Se	^{77}Se	2.0	0.1	0.1	200
Sn	^{118}Sn	1.0	0.02	0.01	200
Mo	^{98}Mo	1.0	0.006	0.01	200
Ag	^{107}Ag	0.25	0.002	0.02	25
Cd	^{111}Cd	0.25	0.01	0.02	200
Cd	^{114}Cd	0.25	0.01	0.01	200
Sb	^{121}Sb	0.5	0.02	0.01	200
Sb	^{123}Sb	0.5	0.01	0.01	200
Ba	^{135}Ba	1.0	0.006	0.03	200
Ba	^{137}Ba	1.0	0.01	0.04	200
Tl	^{205}Tl	1.0	0.01	0.01	200
Pb	^{208}Pb	0.5	0.009	0.05	200
Li	^{6}Li	Inter. Standard			
Sc	^{45}Sc	Inter. Standard			
Ge	^{72}Ge	Inter. Standard			
Rh	^{103}Rh	Inter. Standard			
Y	^{89}Y	Inter. Standard			
In	^{115}In	Inter. Standard			
Tb	^{159}Tb	Inter. Standard			

ENVIRONMENTAL MONITORING DIVISION
Hyperion Treatment Plant - Instrumental Chemistry Strategic Business Unit –
Semi-Volatile Organic Laboratory
STANDARD OPERATING PROCEDURE for

SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

(EPA WASTEWATER METHOD 625)

EMD SOP# 7210

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Laboratory Manager: Lee Huang
Signature:

Quality Assurance Manager: Jeffery Beller
Signature:

TABLE OF CONTENTS

1.0. SCOPE AND APPLICATION

1.1 This method covers the determination of a number of organic compounds that are partitioned into an organic solvent and are amenable to gas chromatography. The parameters listed in Tables 1 and 2 may be qualitatively and quantitatively determined using this method.

1.2 The method may be extended to include the parameters listed in Table 3. Benzidine can be subject to oxidative losses during solvent concentration. Hexachlorocyclo-pentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition. N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described. N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine.

1.3 This is a gas chromatographic/mass spectrometry (GC/MS) method applicable to [2,10] the determination of the compounds listed in Tables 1, 2, and 3 in municipal and industrial discharges as provided under 40 CFR Part 136.1.

1.4 The method detection limit (MDL, defined in Section 16.1) [1] for each parameter is listed in Tables 5. The MDL for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.

1.5 Any modification to this method, beyond those expressly permitted, shall be considered as a major modification subject to application and approval of alternate test procedures under 40 CFR Parts 136.4 and 136.5. Depending upon the nature of the modification and the extent of intended use, the applicant may be required to demonstrate that the modifications will produce equivalent results when applied to relevant wastewaters.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph/mass spectrometer and in the interpretation of

mass spectra. Each analyst must demonstrate the ability to generate acceptable results

with this method using the procedure described in Section 8.

2.0. SUMMARY OF METHOD

2.1 A measured volume of sample, approximately 1 L, is serially extracted with methylene chloride at a pH greater than 11 and again at a pH less than 2 using a separatory funnel or a continuous extractor.[2]

2.2 The methylene chloride extract is dried, concentrated to a volume of 1 mL, and analyzed by GC/MS. Qualitative identification of the parameters in the extract is performed using the retention time and the relative abundance of three characteristic masses (m/z).

2.3 Quantitative analysis is performed using internal standard method with a single characteristic m/z.

2.4 Extraction efficiency is determined by surrogate recoveries and recoveries of laboratory control samples (LCS, analytes spiked in de-ionized water).

3.0. INTERFERENCES

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the total ion current profiles. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.1.3.

3.1.1 Glassware must be scrupulously cleaned.[3] Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Solvent rinsing should be followed by detergent washing with hot water, and rinses with tapw ater and distilled water. The glassware should then be drained dry, and rinsed with acetone and pesticide quality hexane. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize

interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.2 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled.

3.3 The base-neutral extraction may cause significantly reduced recovery of phenol, 2-methylphenol, and 2,4-dimethylphenol. The analyst must recognize that results obtained under these conditions are minimum concentrations.

4.0. SAMPLE COLLECTION, PRESERVATION AND HANDLING

4.1 Sample Bottles.

4.1.1 Samples are collected in glass bottles with Teflon-lined caps. Plastic bottles must not be used since they are known to introduce interferences and absorb pesticides.

4.1.2 The glass bottles are pre-washed with liquid detergent, hot tap water, distilled water, followed by rinsing with hexane.

4.2 Grab samples must be collected in glass containers. Conventional sampling practices[7] should be followed, except that the bottle must not be pre-rinsed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be as free as possible of Tygon tubing and other potential sources of contamination.

4.3 All samples must be iced or refrigerated at 4°C from the time of collection until extraction. Fill the sample bottles and, if residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample and mix well. EPA Methods 330.4 and 330.5 may be used for measurement of residual chlorine. Field test kit (Potassium iodide – starch test paper) are used to test residual chlorine in this method.

4.4 Residual chlorine testing and removal

4.4.1 Moisten Potassium iodide – starch test paper with pH 4 buffer solution and put it into a watching glass.

4.3.1 Place a drop of sample on the moistened Potassium iodide – starch test paper.
If a bluish discoloration is noted, add 80 mg of sodium thiosulfate per liter of sample and mix well before starting extraction.

4.5 Sample receiving: All samples are received and logged into LIMS by Data and Sample Management (DSM) SBU at the Central Receiving Area. When preparation and analysis are needed, samples will be checked out from Central Storage Rooms. After the required volume of samples are taken, samples will be returned to Central Receiving Area for further storage.

4.6 Registering the sample: Samples received in the laboratory are registered in the sample log book where each sample is assigned a unique "sample number" (e.g. Sample Number P-3-3-025; such as P for plant samples, 3 for year 2003, 3 for month March, 025 for sequential number, type of analysis required are assigned by letters; P for pesticides, BNA for Base/Neutral Acids, and V for volatiles. The LIMS login number assigned to each sample by DSM is also recorded in the laboratory log book.

4.7 Sample storage and holding time

4.7.1 Samples are to be stored in a refrigerator at 4 °C.

4.7.2 Extractions for BNA must be performed within 7 days of sample collection for liquid samples.

4.7.3 Extracts must be analyzed within 40 days of the extraction date.

5.0 APPARATUS

5.1. Sampling equipment, for discrete or composite sampling.

5.1.1. Grab sample bottle—1 L, amber glass, fitted with a screw cap lined with Teflon. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The bottle and cap liner must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

5.1.2. Automatic sampler (optional)—The sampler must incorporate glass sample containers for the collection of a minimum of 250 mL of sample. Sample containers must be kept refrigerated at 4°C and protected from light during compositing. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used. Before use, however, the compressible tubing should be thoroughly rinsed

with methanol, followed by repeated rinsings with distilled water to minimize the potential for contamination of the sample. An integrating flow meter is required to collect flow proportional composites.

5.2 Glassware

5.2.1 Separatory funnel—2 L, with Teflon stopcock.

5.2.2 *Funnels and glass wool.*

5.2.3 Concentrator tube, Kuderna-Danish—10 mL, graduated. Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

5.2.4 Evaporative flask, Kuderna-Danish—500 mL. Attach to concentrator tube with springs.

5.2.5 Snyder column, Kuderna-Danish—Three ball.

5.2.6 Vials—1 mL, 10-15 mL, amber glass, with Teflon-lined screw cap.

5.2.7 Continuous liquid-liquid extractor, 250-mL round-bottom flask and condenser — Equipped with Teflon or glass connecting joints and stopcocks requiring no lubrication.

5.3 Heating mantel, temperature controller, and timer.

5.4 Various kinds of gas tight syringes (10 µl, 25 µl, 50 µl, 100 µl, 1000 µl).

5.5 Zymark TurboVap 500 Concentrator, capable of temperature control (2°C).

5.6 VWR Circulating Cooling System.

5.7 Boiling chips—Approximately 10/40 mesh. Heat to 400°C for 30 minutes of Soxhlet extract with methylene chloride.

5.8 Water bath—Heated, with concentric ring cover, capable of temperature control (2°C).The bath should be used in a hood.

5.9 Balance—Analytical, capable of accurately weighing 0.0001 g.

5.10 GC/MS system

5.10.1 Gas Chromatograph—An analytical system complete with a temperature programmable gas chromatograph and all required accessories including

syringes, analytical columns, and gases.

5.10.2 Column—30-m x 0.25-mm I.D. 0.25-µm film thickness silicon-coated fused-silica capillary column (J&W Scientific DB-5).

5.10.3 Mass spectrometer—Capable of scanning from 35-450 amu every seven seconds or less, utilizing a 70 V (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all the criteria in Table 4 when 50 ng of decafluorotriphenyl phosphine (DFTPP; bis(perfluorophenyl) phenyl phosphine) is injected through the GC inlet.

5.10.4 GC/MS interface—Any GC to MS interface that gives acceptable calibration points at 50 ng per injection for each of the parameters of interest and achieves all acceptable performance criteria (Section 8.3.2) may be used. GC to MS interfaces constructed of all glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

5.10.5 Data system—A computer system must be interfaced to the mass spectrometer which is capable of continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for specific m/z and plotting such m/z abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits.

5.10.6 Three HP GC/MSD with HP-ChemStation GCMS software and HP 7673 Autosampler are used :

Instrument Name	Instrument Model	Injection Type
BNA #1	**HP 5890 GC/ 5972 MSD**	**Split/Splitless**
BNA #2	HP 5890 GC/ 5972 MSD	Cool-on-Column
BNA #3	HP 6890 GC/ 5973 MSD	Split/Splitless

6.0. CHEMICALS AND REAGENTS

6.1 Reagent water—Reagent water is defined as a water in which an interferent is not observed at the MDL of the parameters of interest.

6.2 Sodium hydroxide solution (10 N)—Dissolve 40 g of NaOH (ACS) in reagent water and dilute to 100 mL.

6.3 Sodium thiosulfate—(ACS) Granular.

6.4 Sulfuric acid (1+1)—Slowly, add 50 mL of H_2SO_4 (ACS, sp. gr. 1.84) to 50 mL of reagent water.

6.5 Acetone, methanol, hexane and methylene chloride—Pesticide quality or equivalent.

6.6 Sodium sulfate—(ACS) Granular, anhydrous. Purify by heating at 400°C for four hrs in a shallow tray.

6.7 Stock standard solutions—standard solutions are purchased from Supelco.

6.7.1 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just *prior to preparing calibration standards from them.*

6.7.2 Stock standard solutions must be replaced after six months, or sooner if comparison with quality control check samples indicate a problem.

6.7.3 When the working standards are prepared from the stock standards, pertinent information are documented in the standards logbook for BNA.

6.7.4 Following standards are used, 2000 µg/mL each :

Base/Neutrals Mix (cat # 4-7991)

Polynuclear Aromatic Hydrocarbons Mix (cat # 4S8905)

Phenols Mix (cat # 4S8904)

Benzidines Mix (cat # 4S8906)

Hardazdous Substances Mix (cat # 4-7990).

6.8 Surrogate standard spiking solution -- Surrogate standards consisting of six surrogate compounds are purchased from Supelco. Store the spiking solution at 4°C in Teflon-sealed glass container. The solution should be checked frequently for stability. The solution must be replaced after six months, or sooner if comparison with quality control check standards indicates a problem.

6.8.1 Surrogate standards, 4000 µg/mL each in methylene chloride, contains 3 BN and 3 Acid surrogates (cat # 4-7960):

Phenol-d6	Nitrobenzene-d5
2-Fluorophenol	2-Fluorobiphenyl
2,4,6-Tribromophenol	p-Terphenyl-d14

6.9 Internal standard solution— Internal standards consisting of six compounds are purchased from Supelco. Store the spiking solution at 4°C in Teflon-sealed glass container. The solution should be checked frequently for stability. The solution must be replaced after six months, or sooner if comparison with quality control check standards indicates a problem.

6.9.1 Internal standards, 2000 µg/mL each in methylene chloride, contains 6 compounds (cat # 4-8902):

Acenapththene - d10 Naphthalene - d8
Chrysene - d12 Perylene - d12
1,4-Dichlorobenzene - d4 Phenanthrene - d10

6.10 GC/MS Tuning standard— Tuning standard consisting of four compounds is purchased from Supelco. Store the spiking solution at 4°C in Teflon-sealed glass container. The solution should be checked frequently for stability. The solution must be replaced after six months, or sooner if comparison with quality control check standards indicates a problem.

6.10.1 Tuning standards, 50 µg/mL each in methylene chloride, contains 4 compounds (cat # 4-7387):

Pentachlorophenol Decafluorotriphenylphosphine(DFTPP)
Benzidine 4,4'-DDT

6.11 Quality control check Standards— Secondary source standard solutions are purchased from Ultra Scientific, and QC check standard (for Matrix spike and QC spike) are purchased from Supelco.

6.11.1 Secondary source standard solutions:

- Acid Surrogate Std.cat # ISM-295 , 2000 ppm
- Base Surrogate Std.cat # ISM-285, 1000 ppm
- BN Mix #1 Std. cat # US-100N, 2000 ppm
- BN Mix #2 Std. cat # US-101N, 2000 ppm
- PAH Std. cat # US-106N, 2000 ppm
- Phenol Std. cat # US-107N, 2000 ppm
- Benzidine Std. cat # US-105N, 2000 ppm
- Tox. Sub. Mix Std. cat # US-103N, 2000 ppm

6.11.2 QC check standard (for Matrix spike and QC spike):

- BN/PAH Mix Std. cat # 5-02049, 1000 ppm
- Phenol/Benzidine Std. cat # 4-7992-U, 2000 ppm

7.0. SAFETY

7.1 The toxicity or carcinogenicity of each reagent used in this method have not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified for the information of the analyst.[4-6]

7.2 The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzo(a)anthracene, benzidine, 3,3'-dichlorobenzidine, benzo(a)pyrene, dibenzo(a,h)anthracene, and N-nitrosodimethylamine. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

8.0. EXTRACTION PROCEDURES

Prior to extraction, samples should be tested for residual chlorine. Follow the section 4.4 procedure for residual chlorine testing and removal.

8.1. Separatory Funnel Extraction

8.1.1 Samples can be extracted either using separatory funnel technique or continuous extraction (Section 8.2) technique. The separatory funnel extraction scheme described below assumes a sample volume of 1 L.

8.1.2 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2 L separatory funnel. Add the surrogate standard spiking solution into the separatory funnel and mix well. Check the pH of the sample with wide-range pH paper and adjust to pH >11 with sodium hydroxide solution.

8.1.3 Add 50 mL of methylene chloride to the sample bottle, seal, and shake for 30 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for two minutes with periodic venting to release excess pressure. Allow the organic layer to

separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 250 mL Erlenmeyer flask.

8.1.4 Add a second 50 mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner. Label the combined extract as the base/neutral fraction.

8.1.5 Adjust the pH of the aqueous phase to less than 2 using sulfuric acid. Serially extract the acidified aqueous phase three times with 50 mL aliquots of methylene chloride. Collect and combine the extracts in a 250 mL Erlenmeyer flask and label the combined extracts as the acid fraction.

8.1.6 For each fraction, assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 mL concentrator tube to a 500-mL evaporative flask.

8.1.7 For each fraction, pour the combined extract through a solvent-rinsed funnel containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and funnel with 20-30 mL of methylene chloride to complete the quantitative transfer.

8.1.8 Add one or two clean boiling chips and attach a three-ball Snyder column to the evaporative flask for each fraction. Pre-wet each Snyder column by adding about 1 mL of methylene chloride to the top. Place the K-D apparatus on a hot water bath (60-65°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-20 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of methylene chloride. A 5 mL syringe is recommended for this operation.

8.1.9 Combine the acid extract evaporated to about 5 mL into the K-D containing the Base/Neutral extract. Rinse the concentrator used for the acid extract with three portions of methylene chloride of for a total of about 25 mL into the K-D containing Base/Neutral extract. Repeat step 8.1.9 to concentrate the combined extract to 5 mL.

8.1.10 Disconnect the concentrator tube from the evaporation flask. Concentrate by flowing nitrogen gas over the concentrator tube to exactly 1 mL. Put the contents into a 2 mL vial. Do not rinse the concentrator tube into the vial with methylene chloride.

8.1.11 Store in refrigerator at 4 degrees C. Analyze within 40 days.

8.1.12 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000 mL graduated cylinder. Record the sample volume to the nearest 5 mL.

8.2 Continuous Extraction

8.2.1 Assemble vapor recovery system.

8.2.2 Using a 250-mL graduated cylinder, measure 120 mL methylene chloride. (All glassware must be washed with de-ionized water and soap). Next all of the glassware in use should be solvent rinsed once before use and once after use. Collect the solvents in marked solvent waste bottles. Transfer the solvent to the 250 mL round bottom flask and add 3-4 boiling chips.

8.2.3 Connect the flask to an empty extractor. (Do not forget to use Teflon sleeve on the neck for secure connection). Using a 250mL graduated cylinder, measure 120 mL methylene chloride. Transfer the solvent to the extractor.

8.2.4 Using a 1 Liter graduated cylinder, measure 1 liter of sample. Slowly transfer the sample to the extractor using a long neck funnel. Add required spike standards (surrogates, lab control standards, matrix spike and matrix spike duplicate). Adjust the PH of the sample to pH>11 and extract basic extractables with 10 N NaOH.

8.2.5 QC includes one method blank, 1 LCS (Laboratory Control Standard or Blank Spike), 1 Matrix spike per batch. (LCS, MS, should cover at most 20 samples).

8.2.6 All samples should be spiked with Surrogate spiking standard at final concentration of 100 PPM. (50 ul of 2000 ppm BNA Surrogate Spiking Standard).

8.2.7 Industrial waste liquid samples should be spiked at 100 ppm final concentration (50 µl of 2000 ppm BNA Spiking Standard).

8.2.8 Connect vapor recovery system and turn on cooling water.

8.2.9 Timer set up: press **CHANNEL SELECTOR** until **OUTLET** is selected. Then press **OUTLET ON/OFF** to set **OUTLET ON**. Finally enter **180000**(18 Hrs). Press **START** to start timer. Adjust heating mantel controllers to 8. The samples will be extracted for 18 hrs.

8.2.10 After 18 hrs of extraction, adjust the PH of the samples to pH < 2 with Sulfuric Acid

8.2.11 Repeat step 8.2.9 (timer setup) and extract for another 18 hrs more.

8.2.12 After 36 hrs of extraction, the sample is ready for concentration. First pass each extract through a funnel filled with glass wool /Na_2SO_4 and collect the dried extract in Zymark 500mL flask with 1- mL stem. Rinse the round bottom flask and funnel with Methylene Chloride, collect the rinse solvent in the Zymark 500mL flask.

8.2.13 Turn on Zymark TurboVap 500 workstation and VWR circulating cooling system.

8.2.14 Set up the Zymark TurboVap 500 workstation water bath temperature at 48 ^oC and VWR cooling bath at –2 ^oC.

8.2.15 Put the Zymark flask with extracted sample into its place on the TurboVap.

8.2.16 Choose sensor end point on the TurboVap workstation for both samples. Set fan speed at B.

8.2.17 Press start on the TurboVap 500 for both samples.

8.2.18 The TurboVap 500 will stop automatically once it has reached to final volume of 1 mL.

8.2.19 Transfer the samples carefully into pre marked 1-mL vial with 1 mL syringe. If the volume is less than 1 mL, add methylene chloride to 1 mL.

8.2.20 Rinse the Zymark 500mL flask with Methylene Chloride.

8.2.21 Repeat steps 6.12 thru 6.20 again.

9.0. CALIBRATION AND SAMPLE ANALYSIS

9.1 Calibration.

9.1.1. Before the calibration, the GC/MS must be tuned using perfluorotributylamine (PFTBA). The instrument is tuned according to the manufacturer's recommended values. After the tuning is satisfactory, a solution

of decafluorotriphenylphosphine (DFTPP) is injected. The ion abundance must meet the criteria listed in Table 4.

9.1.2 Tailing Factor

9.1.2.1 Include with the DFTPP standard is 50 ng of Benzidine and 50 ng of pentachlorophenol. The tailing factor for benzidine must be calculated as a column maintenance test for the base/neutrals. The benzidine-tailing factor must be less than 3.0.

9.1.2.2. The tailing factor for pentachlorophenol must be calculated as a column maintenance test for the acids. The pentachlorophenol-tailing factor must be less than 5.0. The calculation of tailing factor is illustrated in HP ChemStation software.

9.1.3. Initial Calibration.

9.1.3.1.This should be done when the continuing calibration standard fails.

After conducting the GC/MS performance tests, establish gas chromatographic operating parameters according section 8.3.5. Internal standard calibration procedure is used to calibrate GCMS.

9.1.3.2. To use this approach, the analyst must select three or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standards is not affected by method or matrix interferences. Use the base peak m/z as the primary m/z for quantification of the standards. If interferences are noted, use one of the next two most intense m/z quantities for quantification.

9.1.3.3.Prepare calibration standards at five concentration levels in the range of 1 ng/ul to 100 ng/ul for each parameter of interest by adding appropriate volumes of one or more stock standards to a volumetric flask. To each calibration standard or standard mixture, add a known constant amount of one or more internal standards, and dilute to volume with methylene chloride.

9.1.3.4. A minimum of three-point calibration standard is required in the method. The lowest calibration standard should be at a concentration near, but above, the MDL and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC/MS system. Using injections of 1 μL, analyze each calibration standard and tabulate the area of the primary characteristic m/z against concentration for each compound and internal standard. Calculate response factors (RF) for each compound using Equation 1.

Equation 1 $$RF = \frac{(A_S) * (C_{IS})}{(A_{IS}) * (C_S)}$$

where:

A_S = Area of the characteristic m/z for the parameter to be measured.
A_{IS} = Area of the characteristic m/z for the internal standard.
C_{IS} = Concentration of the internal standard.
C_S = Concentration of the parameter to be measured.

If the RF value over the working range is a constant (<35% RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to construct a calibration curve with the correlation coefficient no less than 0.99.

9.1.4. Continuing calibration verification - After the DFTPP passes the criteria, the mid-point calibration standard is injected. The standard is evaluated against the calibration curve currently in use for quantitation. The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by no more than 20%, analyst can start to analyze samples. If the response for any parameter varies from the predicted response by more than 20%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that compound.

9.1.5 GC/MS operating conditions

9.1.5.1. Instrument Name: BNA #1 (HP 5890 GC/5972 MSD)
Electron energy: 70 eV
Mass range: 35-500 amu
Scan time: 1 sec/scan
Initial column temperature and hold time: 40 °C for 4 min
Column temperature program: 40-270 °C at 10 °C /min
Final column temperature hold: 270 °C (until benzo[ghi]perlene has eluted)

Injector: Grob-type, splitless, 270 °C
Sample volume: 1 µL

Carrier gas: Helium at 1 mL/minute

MS Transfer Line Temperature: 280 °C
MS Source Temperature: 280 °C

9.1.5.2 Instrument Name: BNA #2 (HP 5890 GC/5972 MSD)
Electron energy: 70 eV

Mass range: 35-500 amu
Scan time: 1 sec/scan
Initial column temperature and hold time: 40 °C for 4 min
Column temperature program:
40-270 °C at 10 °C /min
Final column temperature hold: 270 °C (until benzo[ghi]perlene has eluted)
Injector: cool-on-column injection, 230 °C
Sample volume: 1 µL

Carrier gas: Helium at 1 mL/minute

MS Transfer Line Temperature: 280 °C
MS Source Temperature: 280 °C

9.1.5.3 Instrument Name: BNA #3 (HP 6890 GC/5973 MSD)
Electron energy: 70 eV
Mass range: 35-500 amu
Scan time: 1 sec/scan
Initial column temperature and hold time: 50 °C for 0.5 min
Column temperature program: 50-100°C at 10 °C /min
Column temperature program: 100-280°C at 25 °C/min
Column temperature program: 280-300°C at 5 °C/min
Final column temperature hold: 300°C (until benzo[ghi]perlene has eluted)

Injector: Grob-type, splitless, 270 °C

Sample volume: 1 µL
Carrier gas: Helium, Pressure Pulse Program
MS Transfer Line Temperature: 300 °C
MS Source Temperature: 230 °C

9.2 Sample Analysis.

9.2.1. Analyst should keep track of the instrument operating condition.

9.2.2. Calibrate MS with FC43 if necessary.

9.2.3. Document all instrument/software problems and maintenance in the instrument logbook.

9.2.4. Inject 1 ul of 50 ng DFTPP solution.

9.2.5. If DFTPP passes, inject 1 ul of mid-point BNA standard.

9.2.6. If the standard meet the QC criteria stated in this SOP, prepare the extracts for analysis.

9.2.7. The internal standard must be added to sample extract and mixed thoroughly immediately before it is injected into the instrument. This procedure minimizes losses due to adsorption, chemical reaction or evaporation.

9.2.8. Inject 1 µL of the sample extract or standard into the GC/MS system.

9.2.9. If the response for any m/z exceeds the working range of the GC/MS system, dilute the extract and reanalyze.

9.2.10. Perform all qualitative and quantitative measurements as described in Sections 10. When the extracts are not being used for analyses, store them refrigerated at 4°C, protected from light in screw-cap vials equipped with unpierced Teflon-lined septa.

10.0 CALCULATION

10.1 Qualitative Identification

10.1.1. Obtain EICPs for the primary m/z and the two other masses listed in Tables and 5 of EPA Method 625. The following criteria must be met to make a qualitative identification:

- The characteristic masses of each parameter of interest must maximize in the same or within one scan of each other.

- The retention time must fall within 30 seconds of the retention time of the authentic compound.

- The relative peak heights of the three characteristic masses in the EICPs must fall within 20% of the relative intensities of these masses in a reference mass spectrum. The reference mass spectrum can be obtained from a standard analyzed in the GC/MS system or from a reference library.

- Structural isomers that have very similar mass spectra and less than 30 seconds difference in retention time, can be explicitly identified only if the resolution between authentic isomers in a standard mix is acceptable. Acceptable resolution is achieved if the baseline to valley height between the isomers is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

10.2. Calculations.

10.2.1. When a parameter has been identified, the quantitation of that parameter will be based on the integrated abundance from the EICP of the primary characteristic m/z in Tables 4 and 5 of EPA Method 625. Use the base peak m/z for internal and surrogate standards. If the sample produces an interference for the primary m/z, use a secondary characteristic m/z to quantitate.

Calculate the concentration in the sample using the response factor (RF) determined in Section 7.2.2 and Equation 2.

Equation 2 $$\text{Concentration (ug/L)} = \frac{(A_s) * (I_s)}{(A_{is}) * (RF) * (V_0)}$$

where:

A_S = Response for the parameter to be measured.
A_{IS} = Response for the internal standard.
I_S = Amount of internal standard added to each extract (µg).
V_O = Volume of water extracted (L).

10.2.2. Report results in µg/L without correction for recovery data. All QC data obtained should be reported with the sample results.

10.3. Screening Procedure for 2,3,7,8-Tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD)

10.3.1.If the sample must be screened for the presence of 2,3,7,8-TCDD, it is recommended that the reference material not be handled in the laboratory unless extensive safety precautions are employed. It is sufficient to analyze the base/neutral extract by selected ion monitoring (SIM) GC/MS techniques, as follows:

10.3.1.1. Concentrate the base/neutral extract to a final volume of 0.2 mL.

10.3.1.2. Adjust the temperature of the base/neutral column (Section 5.6.2) to 220°C.

10.3.1.3. Operate the mass spectrometer to acquire data in the SIM mode using the ions at m/z 257, 320 and 322 and a dwell time no greater than 333 milliseconds per mass.

10.3.1.4. Inject 5 µL of the base/neutral extract. Collect SIM data for a total of 10 minutes.

10.3.1.5. The possible presence of 2,3,7,8-TCDD is indicated if all three masses exhibit simultaneous peaks at any point in the selected ion current profiles.

10.3.1.6. For each occurrence where the possible presence of 2,3,7,8-TCDD is indicated, the sample are sent to outside lab for high resolution analysis.

10.3.1.7. False positives to this test may be caused by the presence of single or coeluting combinations of compounds whose mass spectra contain all of these masses.

10.3.1.8. Conclusive results of the presence and concentration level of 2,3,7,8-TCDD can be obtained only from a properly equipped laboratory through the use of EPA Method 613 or other approved alternate test procedures.

11.0. QUALITY ASSURANCE AND QUALITY CONTROL

11.1 The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is shown when the analyst meets all QC Aceptance Criteria.

11.2 DFTPP shall be analyzed to confirm that all the key m/z criteria in Table 4 are achieved prior to analysis of samples.

11.3 The initial and CCV standards must meet the QC requirements listed in the calibration section in this SOP.

11.4 A method blank and a LCS(lab control sample, de-ionized water spike) will be analyzed for each batch of samples. A matrix spike (MS) shall be analyzed at the rate of one per 20 samples (5% of samples), on an ongoing basis. If There are less than 20 samples analyzed per month, at least one spiked sample will be analyzed per month.

11.5 The method blank should not have any target analytes at or above the method reporting limit and all surrogates in the method blank should be within the control limit.

11.6 The surrogates in a sample should fall in control range chart(section 11.8). The criteria is no more than one acid and one base/neutral surrogate in a sample can be fallen outside the control limit.

11.7 The spike recoveries of all the analytes in LCS must meet those specified in Table 6 in EPA 625.

11.8 Quality control chart - Quality control chart is a graphical representation of various deviations of data within an interval length of time.

11.8.1 As part of the QC program for the laboratory, method accuracy and precision must be assessed and records must be maintained. On an on–going basis, after the analysis of samples, LCS and spiked wastewater samples, calculate the percent recovery (p), average percent recovery (P) and the standard deviation of the percent recovery (s) for surrogates and spiked analytes . Express the accuracy assessment as a percent interval from -2s to +2s (lower and upper control limit). If P = 90% and s =10%, for example, the accuracy interval is expressed as 70-110%.

11.8.2 Make a quality control chart by plotting RECOVERY (%) vs. NUMBER of spiked wastewater samples or LCS for each analyte, and RECOVERY (%) vs. NUMBER of samples for each surrogate based on accuracy assessment. Update the quality control chart for each parameter on a regular basis: after 5-10 new accuracy measurements, or equivalent to every four months based on the current workload of our lab. In the QC chart, it should have average recovery (P), lower control limit (P – 2s) and upper control limit (P+ 2s), and actual recovery (p) for each analyte.

11.8.3 This QC chart kept in this manner serves as a floating control range chart. This floating control range must be within limits specified by EPA Methodology or corrective actions must be taken.

12.0. REFERENCES

12.1. 40 CFR Part 136, Appendix B. "Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, March 1977, Revised April 1977. Available from Effluent Guidelines Division, Washington, DC 20460.

12.2. ASTM Annual Book of Standards, Part 31, D3694-78. "Standard Practices for Preparation of Sample Containers and for Preservation of Organic Constituents," American Society for Testing and Materials, Philadelphia.

12.3. "Carcinogens-Working With Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.

12.4. “OSHA Safety and Health Standards, General Industry,” (29 CFR Part 1910), Occupational Safety and Health Administration, OSHA 2206 (Revised, January 1976).

12.5. “Safety in Academic Chemistry Laboratories,” American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

12.6. ASTM Annual Book of Standards, Part 31, D3370-76. “Standard Practices for Sampling Water,” American Society for Testing and Materials, Philadelphia.

12.7. “Methods 330.4 (Titrimetric, DPD-FAS) and 330.5 (Spectrophotometric, DPD) for Chlorine, Total Residual,” Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, March 1979.

12.8. Eichelberger, J.W., Harris, L.E., and Budde, W.L. “Reference Compound to CalibrateIon Abundance Measurement in Gas Chromatography-Mass Spectometry,” *Analytical Chemistry,* 47, 995 (1975).

12.9. “EPA Method Study 30, Method 625, Base/Neutrals, Acids, and Pesticides,” EPA 600/4-84-053, National Technical Information Service, PB84-206572, Springfield, Virginia 22161, June 1984.

Table 1—Base/Neutral Extractables

Parameter	STORET No.	CAS No.
Acenaphthene	34205	83-32-9
Acenaphthylene	34200	208-96-8
Anthracene	34220	120-12-7
Benzo(a)anthracene	34526	56-55-3
Benzo(b)fluoranthene	34230	205-99-2
Benzo(k)fluoranthene	34242	207-08-9
Benzo(a)pyrene	34247	50-32-8
Benzo(ghi)perylene	34521	191-24-2
Benzyl butyl phthalate	34292	85-68-7
Bis(2-chloroethyl)ether	34273	111-44-4
Bis(2-chloroethoxy)methane	34278	111-91-1
Bis(2-ethylhexyl)phthalate	39100	117-81-7
Bis(2-chloroisopropyl)ether	34283	108-60-1
4-Bromophenyl phenyl ether	34636	101-55-3
2-Chloronaphthalele	34581	91-58-7
4-Chlorophenyl phenyl ether	34641	7005-72-3
Chrysene	34320	218-01-9
Dibenzo(a,h)anthracene	34556	53-70-3
Di-n-butylphthalate	39110	84-74-2
1,3-Dichlorobenzene	34566	541-73-1
1,2-Dichlorobenzene	34536	95-50-1
1,4-Dichlorobenzene	34571	106-46-7
3,3'-Dichlorobenzidine	34631	91-94-1
Diethyl phthalate	34336	84-66-2
Dimethyl phthalate	34341	131-11-3
2,4-Dinitrotoluene	34611	121-14-2
2,6-Dinitrotoluene	34626	606-20-2
Di-n-octylphthalate	34596	117-84-0
Fluoranthene	34376	206-44-0
Fluorene	34381	86-73-7
Hexachlorobenzene	39700	118-74-1
Hexachlorobutadiene	34391	87-68-3
Hexachloroethane	34396	67-72-1
Indeno(1,2,3-cd)pyrene	34403	193-39-5
Isophorone	34408	78-59-1
Naphthalene	34696	91-20-3
Nitrobenzene	34447	98-95-3
N-Nitrosodi-n-propylamine	34428	621-64-7
Phenanthrene	34461	85-01-8
Pyrene	34469	129-00-0
1,2,4-Trichlorobenzene	34551	120-82-1

Table 2--Acid Extractables

Parameter	STORET No.	CAS No.
4-Chloro-3-methylphenol	34452	59-50-7
2-Chlorophenol	34586	95-57-8
2,4-Dichlorophenol	34601	120-83-2
2,4-Dimethylphenol	34606	105-67-9
2,4-Dinitrophenol	34616	51-28-5
2-Methyl-4,6-dinitrophenol	34657	534-52-1
2-Nitrophenol	34591	88-75-5
4-Nitrophenol	34646	100-02-7
Pentachlorophenol	39032	87-86-5
Phenol	34694	108-95-2
2,4,6-Trichlorophenol	34621	88-06-2
2-methylphenol *	not required	
4-methylphenol *	not required	
2,4,5-Trichlorophenol *	not required	

Table 3—Additional Extractable Parameters a

Parameter	STORET No.	CAS No.	
Benzidine	39120	92-87-5	605
Hexachlorocylopentadiene	34386	77-47-4	612
N-Nitrosodimethylamine	34438	62-75-9	607
N-Nitrosodiphenylamine	34433	86-30-6	607
1,2-Diphenylhydrazine	not required but on NPDES permit		

TABLE 4	
DFTPP KEY IONS AND ION ABUNDANCE CRITERIA	
MASS	ION ABUNDANCE CRITERIA
51	30-60% OF MASS 198
68	<2% OF MASS 69
70	<2% OF MASS 69
127	40-60% OF MASS 198
197	<1% OF MASS 198
198	BASE PEAK, 100% RELATIVE ABUNDANCE
199	5-9% OF MASS 198
275	10-30% OF MASS 198
365	>1% OF MASS 198
441	PRESENT BUT LESS THAN MASS 443
442	>40% OF MASS 198
443	17-23% OF MASS 442

ENVIRONMENTAL MONITORING DIVISION
Hyperion Treatment Plant - Instrumental Chemistry Strategic Business Unit –
Semi-Volatile Organic Laboratory
STANDARD OPERATING PROCEDURE for

CHEMICAL ANALYSIS OF ORGANOCHLORINE PESTICIDES AND PCBS

(EPA Method 608)

EMD SOP# : 7230

Effective Date:	12/09/02
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Pages Revised:	N/A

APPROVAL:
Laboratory Manager: Lee Huang
Signature:

Quality Assurance Manager: Jeff Beller
Signature:

TABLE OF CONTENTS

1.0. SCOPE AND APPLICATION

1.1. This method covers the determination of certain organochlorine pesticides and PCBs. The following parameters can be determined by this method:

	PARAMETER	STANDARD USED
1)	ALDRIN	MIX AB
2)	AROCLOR 1016	INDIVIDUAL
3)	AROCLOR 1221	INDIVIDUAL
4)	AROCLOR 1232	INDIVIDUAL
5)	AROCLOR 1242	INDIVIDUAL
6)	AROCLOR 1248	INDIVIDUAL
7)	AROCLOR 1254	INDIVIDUAL
8)	AROCLOR 1260	INDIVIDUAL
9)	A-BHC	MIX AB
10)	B-BHC	MIX AB
11)	D-BHC	MIX AB
12)	G-BHC	MIX AB
13)	CHLORDANE	INDIVIDUAL
14)	CHLORDANE(5-COMPONENTS)	INDIVIDUAL
15)	DIELDRIN	MIX AB
16)	ENDRIN	MIX AB
17)	ENDOSULFAN I	MIX AB
18)	ENDOSULFAN II	MIX AB
19)	ENDOSULFAN II SULFATE	MIX AB
20)	ENDRIN ALDEHYDE	MIX AB
21)	HEPTACHLOR	MIX AB
22)	HEPTACHLOR EPOXIDE	MIX AB
23)	METHOXYCHLOR	MIX AB
24)	MIREX	MIX AB
25)	O, P'-DDE	MIX AB
26)	O, P'-DDD	MIX AB
27)	O, P'-DDT	MIX AB
28)	P, P'-DDE	MIX AB
29)	P, P'-DDD	MIX AB
30)	P, P'-DDT	MIX AB
31)	TOXAPHENE	INDIVIDUAL

1.2. This is a gas chromatographic (GC) method with dual-column and dual-electron capture detector.

1.3. It is applicable to the determination of the compounds listed above in municipal and industrial discharges as provided under 40 CFR Part 136.1. Compound identification based on the first column analysis will be confirmed on a second column.

1.4. This method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

2.0. SUMMARY OF METHOD

2.1. A measured amount of sample, approximately 1 L, is extracted with methylene chloride using separatory funnel or continuous extraction procedure. The extract is dried and solvent exchanged to hexane during concentration to a volume of 10 ml or less.

2.2. The extract is passed through florisil column (florisil cleanup) to eliminate interferences. Two florisil column fractions, A and B, are collected.

2.3. Elemental sulfur will usually elute entirely in Fraction A of the florisil cleanup. Activated copper powder is used to remove sulfur in Fraction A.

2.4. A Gas Chromatography with dual-column and dual-electron capture detector (ECD) is used to qualify and quantify the samples.

2.5. The calibration curve used is an external standard linear regression not forced through the origin; five points are used for the single component analytes, three points for the multi-component analytes. The lowest calibration concentrations meet The Regional Water Quality Control Board's (RWQCB) Minimum Level requirement. The relative standard deviation of the curve must be less than 10%. Otherwise, a second order fit should be used.

2.6. The minimum detection limits (MDL) were determined by multiplying the standard deviation of seven replicate analyses by t-score value at 99% certainty (40 CFR part 136, appendix B).

2.7. Tentative identifications are obtained by analyzing standards under the same conditions used for samples and comparing resultant GC retention times. Confirmatory information is obtained by comparing the relative response from the two detectors.

3.0 INTERFERENCES

Sources of interference in this method can be grouped into three broad categories.

3.1 Contaminated solvents, reagents, or sample processing hardware.

3.2 Contaminated GC carrier gas, parts, column surfaces, or detector surfaces.

3.3 Compounds extracted from the sample matrix to which the detector will respond.

3.4 Interferences co-extracted from the samples will vary considerably from waste to waste.

4.0. SAMPLE COLLECTION, PRESERVATION, AND HOLDING TIME

4.1. Before use, all sample containers are washed with soap and tap water, rinsed with hexane, then dried. Care must be taken to avoid contact with plastic to minimize phthalate interference in the analyses.

4.2 Liquid samples are collected in 1000 ml or 1gallon-glass bottles with Teflon lined caps. Liquid samples are stored at 4 ^{o}C and must be extracted within 7 days. The extracts must be analyzed within 40 days.

5.0. CHAIN OF CUSTODY AND SAMPLE REGISTRY

5.1. All samples are delivered to the sample Receiving Unit. The samples are logged into LIMS and stored at 4 ^{o}C. The Organic Unit receives samples from the sample-receiving unit for analysis.

5.2. Samples will be logged into organic logbook and a copy of chain of custody will be kept in work order book.

6.0. APPARATUS

6.1. Glassware

- 1000 ml separatory funnel with teflon stopcock and glass stopper
- 125 ml separatory funnel with teflon stopcock and glass stopper
- 1 L beaker
- 250 ml beaker
- 100 mm long-stemmed funnel
- Kuderna-Danish (K/D) flask, 250 ml
- 250 ml round bottom flask
- soxhlet extractor
- graduated ampoule
- ungraduated ampoule
- Snyder column (three ball)
- 500 ml graduated cylinder
- chromatographic column with reservoir
- 5 ml vials with teflon septa
- 2 ml vials with teflon septa
- centrifuge bottles
- dispensing flask

6.2. Equipment

- Shake
- Double beam balance
- Centrifuge
- Waterbath
- Solvent evaporation unit
- Nitrogen stream evaporation unit
- Waterbath
- Glass wool
- Boiling chips (soxhlet extracted or put in furnace at 400^0C)
- Clamps (various sizes)
- Tweezers
- Thimbles

6.3 Gas Chromatograph

6.3.1 Analytical system complete with programmable GC suitable for organochlorine pesticides and PCBs analyses and all required accessories, including a data system for measuring peak heights and areas.

6.3.2 GC columns: a) DB-5 or similar type, 30m 0.32mm ID, 0.25 um film thickness; b) DB-1701 or similar type, 30m 0.32mm ID, 0.25 um film thickness.

6.3.3 The following GC/ECD systems are available for Pesticides and PCBs analyses:
A. **HP 5890 GC-ECD**
B. HP 6890 GC-ECD
C. Varian 3800 GC-ECD #1
D. **Varian 3800 GC-ECD #2**

6.3.3.1.**Gas Chromatograph- HP 5890**
Data station with Window NT and HP ChemStation Enviroquant software
Dual Electron Capture Detectors
Autosampler (HP 7673)
Columns:
Primary: DB5-60 m length, 0.32 mm diameter.
Confirmation: DB-XLB 60 m length, 0.32 mm diameter.

On Column Dual Injection (two independent injectors)
HP LaserJet 4 printer

HP5890 Temperature Program for All Samples:

Detector Temperature: 300 ^{O}C

Injector Temperature: 250 ^{O}C

Oven Program:

Initial Temperature 120 ^{O}C
Initial Time 0.5 Minutes

Level	Rate (C/min)	Final Temp (^{O}C)	Final Time (min)
1	5.0	160	0.00
2	3.0	260	3.0

Total Program Time: 44.83 Minutes

Inlet A Pressure Values:

Constant Flow: On
Pressure: 267 kpa
Temperature 120 ^{O}C

Inlet B Pressure Values:

Constant Flow: On
Pressure: 111 kpa
Temperature: 120 ^{O}C

6.3.3.2. **Gas Chromatograph- HP 6890**

Data station-Kayak with Windows NT and HP ChemStation Enviroquant software
Electron Capture Detector
Autosampler (HP 6890 series)
Columns:
Primary: HP-5 30m length, 0.320-mm id.
Confirmation: DB-1701 30m length, 0.320-mm id.
Dual Injectors – fast inject
HP LaserJet 4000 printer

HP6890 Temperature Program for All Samples:
Detector Temperature: 300 ^{O}C
Oven Program:
Initial Temperature: 100 ^{O}C
Initial Time: 2.0 Minutes

Level	Rate (^{O}C /min)	Final Temp (^{O}C)	Final Time (min)
1	8.0	160	0.00
2	2.0	265	5.00

Total Program Time: 67.0 Min

Inlet Temperature/Pressure Information for Both Inlet A and B:

Initial Temperature: 250 ^{O}C (On)
Initial Time: 2.0 Minutes
Mode: Pulsed Splitless
Pressure: 63.4 kpa (On)-Injector A
Pressure: 56.4 kpa (On)-Injector B
Pulse Pressure: 172 kpa
Pulse Time: 0.75 min.
Purge Flow: 0.75 mL/min
Total Flow: 64.0 mL/min(A); 63.9 mL/min(B)
Gas Saver: On
Saver Flow: 20 mL/min
Saver Time: 3.00 min
Gas Type: Helium

Pressure Program:

GC Pressure Units: kpa
Entered Values:
Column Length: 30m
Column Diameter: 0.320 mm
Gas: Helium
Vacuum Comp: Off

Column 1	Column 2
Hp-5 5% Methyl Siloxane	DB-1701
Mode: Constant Flow	Mode: Ramped Flow
Initial flow: 1.5 mL/min	Initial flow: 1.3 mL/min
Nominal Initial Pressure: 63.4 kpa	Nom. Initial Pressure: 56.4 kpa
Average Velocity: 29 cm/sec	Average Velocity: 26 cm/sec

Ramped Flow Program for Column 2

#	Rate	Final Flow	Final Time
1	40.00	5.0	5.00
2	40.00	1.0	28.00
3	0.0 (Off)		

Post Flow: 0.0 mL/min

Data station-Kayak with Windows NT and HP ChemStation Enviroquant software

Electron Capture Detector
Autosampler (HP 6890 series)
Columns:
Primary: HP-5 30m length, 0.320-mm id.
Confirmation: DB-1701 30m length, 0.320-mm id.

Dual Injectors – fast inject
HP LaserJet 4000 printer

HP6890 Temperature Program for All Samples:

Detector Temperature: 300 ^{O}C
Oven Program:
Initial Temperature 100 ^{O}C
Initial Time 2.0 Minutes

Level	Rate (^{O}C /min)	Final Temp (^{O}C)	Final Time (min)
1	8.0	160	0.00
2	2.0	265	5.00

Total Program Time: 67.0 Min

Inlet Temperature/Pressure Information for Both Inlet A and B:

Initial Temperature 250 ^{O}C (On)
Initial Time 2.0 Minutes
Mode: Pulsed Splitless
Pressure: 63.4 kpa (On)-Injector A
Pressure: 56.4 kpa (On)-Injector B
Pulse Pressure: 172 kpa
Pulse Time: 0.75 min.
Purge Flow: 0.75 mL/min
Total Flow: 64.0 mL/min(A);63.9 mL/min(B)
Gas Saver: On
Saver Flow: 20 mL/min
Saver Time: 3.00 min
Gas Type: Helium

Pressure Program:

GC Pressure Units: kpa
Entered Values:
Column Length: 30m
Column Diameter: 0.320 mm
Gas: Helium

Vacuum Comp: Off

Column 1	Column 2
Hp-5 5% Methyl Siloxane	DB-1701
Mode: Constant Flow	Mode: Ramped Flow
Initial flow: 1.5 mL/min	Initial flow: 1.3 mL/min
Nominal Initial Pressure: 63.4 kpa	Nom. Initial Pressure: 56.4 kpa
Average Velocity: 29 cm/sec	Average Velocity: 26 cm/sec

Ramped Flow Program for Column 2

#	Rate	Final Flow	Final Time
1	40.00	5.0	5.00
2	40.00	1.0	28.00
4	0.0 (Off)		

Post Flow: 0.0 mL/min

6.3.3.3. Gas Chromatograph- Varian 3800 GC-ECD

Data station- Varian STAR Chromatography Workstation 5.52 with Windows NT
Electron Capture Detector
Autosampler (Varian CP-8400)
Columns:
Primary: DB-5 60m length, 0.320-mm id.
Confirmation: DB-1701 60m length, 0.320-mm id.

Dual Injectors – Varian 1079 Variable Temperature Injector
HP LaserJet 4100 printer

HP6890 Temperature Program for All Samples:

Detector Temperature: 300 ^{O}C
Oven Program:
Initial Temperature 70 ^{O}C
Initial Time 2.3 Minutes

Level	Rate (^{O}C /min)	Final Temp (^{O}C)	Final Time (min)
1	15.0	170	0.00
2	4.0	220	0.00
3	2.0	265	5.00

Total Program Time: 48.97 Min

Inlet Temperature/Pressure Information for Both Inlet A and B:

Initial Temperature 250 ^{O}C (On)
Initial Time 2.0 Minutes
Mode: Pulsed Splitless
Injector A (EFC Type 1): Constant Column Flow is 3.6 ml/min
Pulse Pressure: 60.0 psi
Pulse Duration: 2.30 min
Injector B (EFC Type 1): Constant Column Flow is 3.4 ml/min
Pulse Pressure: 60.0 psi
Pulse Duration: 2.30 min
Gas Type: Helium

Column 1	Column 2
DB-5 5% Methyl Siloxane	DB-1701
Mode: Constant Flow	Mode: Constant Flow
Flow: 3.6 mL/min	Initial flow: 3.4 mL/min
Initial Pressure: 60 psi	Initial Pressure: 60 psi

7.0. CHEMICALS AND REGEANTS

7.1. Chemicals

- Hexane - pesticide grade
- Methylene Chloride - pesticide grade
- Acetone
- acetonitrile
- Ethyl ether - pesticide grade
- Florisil (60/100 mesh)
- Sodium sulfate (granular)
- Copper (granular)

7.2. Standards

7.2.1 All calibration standards should be at least 96% pure and are generally purchased ChemService (primary standards). Second source standards and LCS spike standards are purchased from Ultra Scientific. All standards are prepared in hexane except LCS spiking standards (in methanol), with volumetric flasks and stored in amber bottles with Teflon lined caps at 4 ^{0}C.

7.2.2 Five calibration concentrations are prepared for each standard or set of standards. New standards are prepared within 6 months (or sooner if signs of degradation are apparent). Newly prepared standards are compared with second source standards. If they are not within 20%, the standards are verified against a third source.

7.2.3 See Attachment for standard preparation.

8.0. EXTRACTION

8.1. All samples undergoing extraction are entered into the extraction logbook. This book contains the sample log number, date extraction started, date extraction finished, spike amount, date of florisil, sulfur clean up, final volume, date concentrated, and initials of person conducting extraction.

8.2. EMD follows both liquid-liquid manual extraction and automated continuous Extraction procedure. Please refer to Appendix - A for Continuous Extraction.

8.3 Liquid - Liquid Manual Extraction procedure:

a. Rinse the following glassware with hexane: separatory funnel, long-stemmed funnel, graduated cylinder, K/D flask, ampoule.

b. Using stainless steel tweezers, place a small amount of glass wool in the long-stemmed glass funnel.

c. Place approximately 100 grams of sodium sulfate over the glass wool and rinse with methylene chloride.

d. Connect the K/D and ampoule with a blue plastic clamp and position them underneath the glass funnel with the tip protruding approximately one inch into the K/D.

e. Attach a stopcock to the separatory funnel and place on a ring stand.

f. Label the separatory funnel and K/D with the name of the sample and the log number.

g. Pour 500ml of a well-mixed sample into the graduated cylinder.

h. Carefully pour the sample into the separatory funnel (use a funnel if necessary) and rinse the graduated cylinder with three 10ml portions of distilled water.

i. Spike each sample with surrogate and add pesticide spike to samples assigned for QC. (Ask the chemist to do the spiking).

j. Rinse the graduated cylinder with two 25ml, portions of methylene chloride and pour into the separatory funnel.

k. Stopper the separatory funnel, invert, and vent immediately (always vent into the fume hood).

l. Shake a few times and vent again. Continue this step until the pressure has been released.

m. Place the separatory funnel on the mechanical shaker and shake for two minutes.

n. After removal, wait at least ten minutes for the organic and aqueous layers to separate. If no emulsion layer is formed, proceed with step p.

o. If an emulsion is present, continue with the following steps:

i. Drain the emulsion into a previously rinsed centrifuge bottle. Using another centrifuge bottle (filled with water or another sample) to balance the two bottles by adjusting the weight with distilled water.

ii. Place the bottles on opposite sides in the centrifuge and centrifuge the samples approximately ten minutes.

iii. Slowly pour the sample back into the separatory funnel using a Funnel if necessary. Rinse the centrifuge bottle with three 10ml portions of distilled water.

p. Drain the organic layer into the K/D flask through the funnel containing sodium sulfate.

q. Add 50ml of methylene chloride to the separatory funnel.(If the sample was centrifuged, rinse the centrifuge bottle with two 25ml portions of methylene chloride and pour into the separatory funnel).

r. Repeat steps k-q for second extraction.

s. Repeat steps k-q for third extraction.

t. Discard the water layer and rinse the separatory funnel with 3 10 ml portions of methylene chloride. Drain each portion through sodium sulfate into the K/D flask.

u. Put 1-2 boiling chips into the K/D and adjust the water temperature to 65-70^{0}C.

v. Rinse the Snyder column with approximately 5ml of methylene chloride and connect to the K/D.

w. Connect the K/D and Snyder column to the distillation unit. The water level must be below the connection of the K/D to the ampoule.

v. Concentrate the sample to approximately 8-10ml and cool for a few minutes.

y. Add 25ml of hexane to the K/D through the top of the Snyder column (solvent exchange) and add another boiling chip. Adjust temperature to 80-85oC.

z. Concentrate the sample to approximately 8-10ml. After cooling, stopper the ampoule and place it in the refrigerator until the florisil cleanup can be started.

9.0 FLORISIL AND SULFUR CLEANUP

Refer to the Appendix B for Florisil and Sulfur Cleanup Procedures.

10.0. GAS CHROMATOGRAPH

10.1 Documentation

Analyst will write his/her initial and date in extraction logbook before analysis starts. The raw data, originally stored on the hard disk, is transferred to Virtual Drive for long term storage.

10.2 Instrument set up

see 6.3

10.3. Calibration

10.3.1 Initial calibration for single component analytes (Pesticides and 5 chlordane congeners)

10.3.1.1 The external standard calibration procedure is used. Initial calibration is performed by using 5 concentration levels for single component analytes. The acceptance criteria for the initial calibration is that the relative standard deviation (%RSD) of the calibration factors less than 10%.

$$CF = \frac{A}{C}$$

$$\text{Mean } CF = \overline{CF} = \sqrt{\frac{\sum_{i=1}^{n} \{CF_i - \overline{CF}\}^2}{n-1}}$$

$$\%\text{RSD} = \overline{SD} * 100 / CF$$

$\overline{CF}$ = average calibration factor
A - Peak area of the compound in the standard
C – Concentration of the compound
SD = standard deviation of calibration factors
CF = calibration factor

10.3.1.2 Average calibration factor is used to calculate unknown concentration in samples.

10.3.1.3 A second order fit calibration curve is used if %RSD > 10%.

10.3.2 Initial calibration for multiple-components analytes(Chlordane, Toxaphene and Aroclors)

10.3.2.1 The external standard calibration procedure is used. Initial calibration is performed by using 3 concentration levels.

10.3.2.2 7 to 10 characteristic peaks are chosen for calibration.

10.3.2.3 The acceptance criteria for the initial calibrations is that the percent relative standard deviation(%RSD) of the calibration factors is less than 10% for each of the characteristic peaks.

10.3.2.4 A second order fit calibration curve is used if %RSD > 10%.

10.3.3 Daily Calibration for single components

10.3.3.1 The working calibration curve must be verified on each working day by injection of one or more of the calibration standards. The mid-point concentration from the five point curve is used as the continuing calibration standard and is analyzed at the beginning of each working day.

10.3.3.2 The acceptance criteria for the daily calibration is that the %RPD (relative percent difference), must be < 15% before any sample is analyzed.

$\%RPD = |CF - \overline{CF}| * 100 / \overline{CF}$

10.3.4 Daily calibration for multiple peak components (Chlordane, Toxaphene and Aroclors)

10.3.4.1 The working calibration curve must be verified on each working day by injection of one or more of the calibration standards. The mid-point concentration from the three point curve is used as the continuing calibration standard and is analyzed at the beginning of each working day.

10.3.4.2 The acceptance criteria for the daily calibration is that the %RPD (relative percent difference), must be <%15 before any sample is analyzed.

10.4 GC operation (samples)

10.4.1 Calibration is checked by analyzing mid-point standard and meeting the criteria in 10.3.3 and 10.3.4 before sample analysis is continued.

10.4.2 Inject a 1-µL aliquot of the concentrated sample extract. Record the volume injected and the resulting peak size in area units.

10.4.3 Qualitative identifications of target analytes are made by examination of the sample chromatograms, as described in Section 11.

10.4.4 Quantitative results are determined for each identified analyte, using the procedures described in section 11. If the responses in the sample chromatogram exceed the calibration range of the system, dilute the extract and reanalyze.

10.4.5 In an autosampler run, hexane is run after at least every 15 samples or less to check for carryover.

11.0 IDENTIFICATION

11.1 Target analytes are identified by comparing the retention time of the peaks in the sample chromatogram with those of the peaks in standard chromatograms. The width of the retention time window used to make identification should be based upon measurement s of actual retention time variations of standards (mean $\pm$ 3 x standard

deviation). All analytes identified in primary column must be confirmed on the second column.

11.2 For single component analytes, positive hits on the primary column must be confirmed on the second column.

11.3 Following criteria are used to identify multi-component analytes:

11.3.1 At least 5 of the characteristic peaks must be within plus or minus three times the standard deviation of the retention time of their corresponding peak in the standard.

11.3.2 The pattern in the sample chromatogram should be compared to that of the standard to ensure that all the major components in the standard are present, and ratio of the peaks in the sample to those in the standard should be consistent within the limitations imposed by the matrix.

11.3.3 For Aroclors, comparing the sample chromatogram to that of the most similar Aroclor standard. A choice must be made as to which Aroclor is most similar to that of the residue and whether that standard is truly representative of the PCBs in the sample.

12.0 QUANTITATION

12.1 Quantitation of single component analytes:

Average response factor (RF) or calibration factor (CF) from initial calibration is used for quantitation of target compounds. A second fit calibration curve can be used if %RSD greater than 10%. Positive hits on the primary column must be confirmed on the second column within $\pm$ 50% of primary column results. Since it is possible for analytes to be present and be outside the confirmation acceptance criteria, the analyst should weigh heavily in the interpretation of chromatogram.

12.2 Quantitation of multipeak components (Chlordane, Toxaphene and Aroclors):

After running and reprocessing the chromatogram of the sample to be analyzed, the concentration of 5-7 peaks of the 7-10 characteristic peaks chosen in the initial calibration that are closest in value for the sample are added together and the mean is calculated. This mean value is reported as the analytical result of the analysis for the given multipeak component. The reason for choosing the 5-7 closest of the 7-10 results is that in samples that are extremely dirty and/or those that have complex matrices, there invariably occurs some co-elution of other components or of unidentified peaks in the matrix with at least one or two of the peaks selected for quantitation. The choice of the 5-7 closest peaks removes some of the variation in value caused by co-elution and

matrix interference. Positive hits on the primary column must be confirmed on the second column within ± 50% of primary column results.

13.0. DATA PROCESSING

The data from the GC run must be reprocessed. This reprocessing includes setting the integration events to draw baselines properly on the chromatogram. In some cases manual integration will be necessary to insure that everything is integrated correctly. Make sure that the data station will calculate the results using average response factors of the 5-point calibration curve.

14.0. QC PROCEDURE

14.1 Blank and Laboratory Control Samples (LCS)

14.1.1 Method Blank
14.1.2 LCS – Pesticide (0.3 µg/L)
14.1.3 LCS – Mixture of Aroclor 1016 and 1260 (4 µg/L)
14.1.4 LCS – Toxaphene (5 µg/L)
14.1.5 LCS – Chlordane (2 µg/L)
14.1.6 LCS – 5 Chlordane Congeners (for certain samples, 0.3 µg/L)

14.2 Matrix Spikes (MS): spike concentrations are the regulatory concentration limit.

14.2.1 Matrix Spike – Pesticides (0.05 µg/L)
14.2.2 Matrix Spike – Mixture of Aroclor 1016 and 1260 (2.5 µg/L)

14.3 Frequency

14.3.1 A method blank and a set of LCS are analyzed with every batch of sample.
14.3.2 10% of all samples are spiked with Pesticides and PCBs.
14.3.3 Surrogate standards are added to blank, LCS and samples before extraction (0.4 µg/L).

14.4 Spike information is recorded in the pesticide and PCBs extraction logbook.

14.5 The method blank must be below the ML of the method. No blank values will be subtracted from the sample value.

14.6 The percent relative standard deviation (%RSD) of the calibration curve must be below 10% in order to use the average calibration factor; if the %RSD is greater than 10%, a second fit order fit is used.

14.7 Continuing calibration standard is analyzed after every 20 samples and the end of the analytical sequence. If the results of a continuing calibration standard are

between 85% - 115% of the expected value, the initial calibration curve is verified. If the continuing calibration results exceed these criteria, all samples after the failing continuing calibration must be re-analyzed.

14.8 Results may be reported from either column of the dual column system, provided that all QC criteria are met on the column used for reporting.

14.9 LCS recoveries must be within limits specified in Table 3 of EPA Method 608. QC charts for LCS are updated every 5 – 10 batches of analysis.

14.10 MS and surrogate recoveries must be monitored with limits calculated using historical data (QC chart). QC charts for LCS are updated every 5 – 10 batches of analysis.

14.11 If the primary column results for a LCS exceed the QC criteria, the results from the second column may be used. If both LCS results fail, the LCS must be re-analyzed at once. If the repeat analysis also fails, sample batch must be re-extracted.

14.12 Any sample that has a positive result greater than the value of the highest standard must be diluted and re-analyzed.

14.13 Positive hits on the primary column must be confirmed on the second column within $\pm$ 50% of primary column results. Since it is possible for analytes to be present and be outside the confirmation acceptance criteria, the analyst should weigh heavily in the interpretation of chromatogram.

14.14 Data package must include:

14.14.1 All reports and chromatograms for all runs in analytical sequence including initial and continuing calibration data.

14.14.2 Copy of data system method and sequence files.

14.14.3 %RSD determination for the calibration curves.

14.14.4 Retention time window determination for primary and secondary columns.

14.14.5 Sample preparation log sheet.

14.14.6 Filled reporting forms (for samples, blank, LCS and MS).

14.14.7 LIMS workgroup report and RUN ID.

14.15 Solutions from which spiking solutions are made need to be purchased either from a different manufacturer than the one from which Standard solutions are made, or

from a different lot# from the same manufacturer. In addition, a 3rd set of solutions should be available, such as ERA or EPA standard solutions. These solutions can be used to check the accuracy of the solutions obtained from other manufacturers.

APPENDIX-F1

Standard Operating Procedure
For Continuous Liquid-Liquid Extraction of Pesticides and PCBs

1.0 SCOPE AND APPLICATION

1.1 This method is based on EPA Wastewater Method 608 – Continuous Liquid – Liquid Extraction Section.

1.2 This method describes a procedure for isolating organic compounds from aqueous samples, Pesticides and PCBs.

1.3 This method is applicable to the isolation and concentration of water-insoluble and slightly soluble organics in preparation for a variety of chromatographic procedures.

1.4 This method is designed for extraction solvents with a greater density than samples.

2.0 SUMMARY OF METHOD

2.1 A measured volume of sample, usually 1 liter, is placed into a continuous liquid-liquid extractor, and extracted with methylene chloride for 18 hours. The extract is dried, concentrated, and exchanged into hexane for further cleanup.

3.0 APPARATUS AND MATERIALS

3.1 Stands, Clamps and rings.
3.2 Continuous liquid-liquid extractor.
3.3 Solvent vapor recovery system.
3.4 Heating mantle, heating mantle controller, and time controller.
3.5 Boiling chips.
3.6 Kudema-Danish apparatus: concentrator tube (10-ml), distilling flask (250-ml), clamp, and Snyder column.
3.7 Vials (5-ml) and Teflon-lined screw caps.
3.8 Funnels and glass wool.

4.0 REAGENTS

4.1 All Reagents used in extraction should be Pesticide-Grade.
4.2 Organic-free Water.
4.3 Sodium sulfate (granular, anhydrous).
4.4 Methylene chloride.

4.5 Hexane.

5. PROCEDURE

5.1 Assemble vapor recovery system.

5.2 Using 250-ml graduated cylinder, measure 120-ml methylene chloride. Transfer the solvent to 250-ml distilling flask and add 3-4 boiling chips.

5.3 Connect the flask to an empty extractor.

5.4 Using 250-ml graduated cylinder, measure 120-ml methylene chloride. Transfer the solvent to the extractor using longneck funnel.

5.5 A 1-liter graduated cylinder, measure 1 liter of sample. Slowly transfer the sample to the extractor using longneck funnel.

5.6 Spike surrogate spiking solution into each sample. Spike matrix-spiking standards if necessary.

5.7 Connect vapor recovery system, and turn on cooling water.

5.8 Timer setup: press **CHANNEL SELECTOR** until **OUTLET** is selected. Press **OUTLET ON/OFF** to select **OUTLET ON**. Enters **180000** (18 hours).

5.9 Press **START** to start timer. Adjust heating mantle controllers to 8.

5.10 After Extracting sample for 18 hours, allow extractor to cool, detach the extractor with the distilling flask from the condenser. Slightly leans the extractor in the flask direction to remove the remaining methylene chloride from the extractor to the flask. Avoid getting water in the flask.

5.11 Assemble a Kudema-Danish (K-D) concentrator by attaching a 10-ml concentrator tube to a 250-ml evaporation flask.

5.12 Dry the extract by passing it through anhydrous sodium sulfate in a longneck funnel with glass wool. Collect the dried extract in a K-D concentrator. Rinse the sodium sulfate with 20-30 ml of methylene chloride and collect it in K-D concentrator.

5.13 Add one or two clean boiling chips to the flask and attach a Snyder column. Place the K-D apparatus on a 65 – 70 ^{o}C water bath to concentrate the extract to less 10 ml. Remove the K-D apparatus from the water bath.

5.14 Pour 30 ml hexane onto the of the Snyder column. Concentrate the extract to less 10 ml on an 85 – 90 ^{o}C water bath.

5.15 Remove the K-D apparatus and allow it to cool, and remove the Snyder column. The extract may be further concentrated by Nitrogen blow down technique or ready for further cleanup.

APPENDIX-F2

FLORISIL AND SULFUR CLEANUP PROCEDURE

1. Scope and Application:

   The following procedure covers the cleanup of liquid and solid samples for pesticides and PCB's.

2. Summary of Method:

A measured volume of sample is extracted with methylene chloride and solvent exchanges with hexane. A florisil cleanup followed by sulfur cleanup step is used to reduce interference.

3. Apparatus and Materials:

3.1. Glassware

1. 1 Liter and 2-Liter Separatory Funnel with teflon stopcock and glass stopper.
2. 100mm long-stemmed funnel
3. Kuderna-Danish (K/D) flask 250ml
4. Ungraduated ampule (15ml)
5. Snyder Column (Three-ball)
6. 500ml graduated cylinder
7. Chromatographic column with reservoir
8. 5ml vials with teflon-lined screw caps
9. Centrifuge bottle
10. Dispensing flasks
11. Stirring rods

3.2. Reagents

1. Pesticide grade methylene chloride
2. Pesticide grade hexane
3. Pesticide grade sodium sulfate
4. Florisil (60/100 mesh)
5. Pesticide grade ethyl ether

3.3. Equipment

1. Shaker
2. Mettler or Ohaus Balances

3. Centrifuge
4. Waterbath
5. Solvent evaporation unit
6. Nitrogen stream evaporation unit

3.4. Miscellaneous Materials

1. Glasswool
2. Boiling chips (soxhlet extracted or put in furnace at 400^0C)
3. Clamps (various sizes)
4. Tweezers
5. Baker analyzed granular copper

4. Procedure:

4.1. Florisil Cleanup (A and B fractions):

Summary: The pesticides extracts will be separated into fractions by eluting with two ether/hexane compositions. The sample is eluted with 200 ml each of 6% ether/hexane (fraction A) first, then 50% ether/hexane (fraction B), and fraction A and B are concentrated to a final volume of 10 ml respectively for liquid samples; 5 ml respectively for solid samples.

Sample extracts (Methylene Chloride) should be solvent exchanged to Hexane before Florisil Cleanup.

4.1.1. Remove the florisil from the 130-degree oven, and let it cool down.

4.1.2. Rinse the chromatographic column, K/D, graduated ampule, stopcock, and tip with hexane.

4.1.3. Insert a small amount of glasswool at the bottom of the column, and connect the stopcock and tip to the column.

4.1.4. Pour 50ml of hexane to the column.

4.1.5. Add the corresponding amount of Florisil from the pre-marked pharmaceutical graduated cylinder into the column. (EPA 3620-5 recommends 20.0 grams florisil).

4.1.6. Tap the column to settle the florisil. Add about a 15-mm layer of anhydrous sodium sulfate to the top (rinsing down the sides of the column with hexane).

4.1.7. Drain the column until the solvent layer is approximately 5-mm above the sodium sulfate (discard the hexane).

4.1.8. Attach the K/D and ampule underneath the column with the tip protruding into the K/D.

4.1.10. Retrieve the previously extracted and solvent exchanged sample from the refrigerator and pour into the column using a funnel. Stopper the ampule and temporarily set it aside.

4.1.11. Adjust the stopcock to elute at a rate of 2 drops/second.

4.1.12. Before the extract level reaches the top of the sodium sulfate (before exposing sodium sulfate layer to air), rinse the above ampule 3 times using a total of 25 ml hexane, and pour the rinse into the column.

4.1.13. When the solvent has reached the top of the sodium sulfate again, add 25 ml of 6% ether/hexane rinsing the ampule as in step 12.

4.1.14. After the solvent level has reached the top of the sodium sulfate again, add 75 ml of 6% ether/hexane. If necessary, adjust the stopcock to maintain the 2 drops/second rate.

4.1.15. Repeat step 14 adding 100 ml of 6% ether/hexane instead of 75 ml. Close the stopcock when the solvent level reaches the top of the sodium sulfate. This is the "A" fraction.

4.1.16. Remove the K/D set-up, add few boiling chips and place it in the water bath. Adjust the temperature of the water bath to 80-85 ^{o}C and begin concentrating the "A" fraction. Remove the K/D from the water bath once the sample volume is lowered to 8 to 10 ml. Make final volume 10 ml for liquid samples, 5 ml for solid samples.

4.1.17. Place another K/D under the Florisil column to collect the "B" fraction.

4.1.18. Add 100 ml of 50% ether/hexane to the column and adjust the flow rate to 2 drops/second.

4.1.19. When the solvent from step 17 reaches the top of the sodium sulfate, add a second 100 ml of 50% ether/hexane. After the solvent reaches the top of the sodium sulfate, close the stop- cock. This is the B fraction.

4.1.20. Repeat step 16 for the B fraction.

4.1.21. Wipe the water from the ampule-K/D connection and remove the ampule from the K/D. Allow the ampule to cool. Using a stream of nitrogen gas, concentrate the A and B extracts to exactly 10 ml. (If the solvent level goes below 10 ml, add hexane dropwise until the level is brought back to 10 ml. NOTE: When

concentration is completed, turn off the main valve on the Nitrogen tank as a conservation measure.

4.1.21 For "B" fractions, pour the extract into a vial (one that has been hexane rinsed and dried), cap and place in appropriate box in the refrigerator. 10 ml for liquid samples,

4.1.23. Conduct sulfur clean-up on "A" fractions only. (Refer to the Sulfur Clean-Up Procedure bellow), transfer to a 5ml vial and place in appropriate box in refrigerator.

4.2. SULFUR CLEAN UP PROCEDURE:

4.2.1. Measure approximately 2 grams of copper granules for each sample to be sulfur-cleaned and transfer it to a 125-ml separatory funnel.

4.2.2. Add enough of 6N HCl to soak all the copper completely, shake it slowly for 30 seconds and discard the HCl.

4.2.3. Wash the copper with methanol a few times until the methanol passes through without discoloration.

4.2.4. To remove the methanol, wash the copper a few times with hexane until it passes through without further discoloration.

4.2.5. Dry the copper under Nitrogen stream and transfer to a 5 ml vial.

4.2.6. Using a Coors #02 porcelain spatula, transfer one spoonful of the activated copper to a 5 ml vial and add the concentrated A fraction from step 21.

4.2.7. Shake on a vortex for 2 minutes, if the copper turns dark, repeat step 6 until there will be no further discoloration.

4.2.8. Transfer the Sulfur-cleaned sample to a clean 5 ml vial and store in proper box in refrigerator.

NOTE: If any excess activated copper in hexane remains, do not discard. But save and add it to the next batch of copper to be activated.

Table 1.

PARAMETER	STANDARD USED
1) ALDRIN	MIX AB
2) AROCLOR 1016	INDIVIDUAL
3) AROCLOR 1221	INDIVIDUAL
4) AROCLOR 1232	INDIVIDUAL

5)	AROCLOR 1242	INDIVIDUAL
6)	AROCLOR 1248	INDIVIDUAL
7)	AROCLOR 1254	INDIVIDUAL
8)	AROCLOR 1260	INDIVIDUAL
9)	A-BHC	MIX AB
10)	B-BHC	MIX AB
11)	D-BHC	MIX AB
12)	G-BHC	MIX AB
13)	CHLORDANE	INDIVIDUAL
14)	CHLORDANE(5-COMPONENTS)	INDIVIDUAL
15)	DIELDRIN	MIX AB
16)	ENDRIN	MIX AB
17)	ENDOSULFAN I	MIX AB
18)	ENDOSULFAN II	MIX AB
19)	ENDOSULFAN II SULFATE	MIX AB
20)	ENDRIN ALDEHYDE	MIX AB
21)	HEPTACHLOR	MIX AB
22)	HEPTACHLOR EPOXIDE	MIX AB
23)	METHOXYCHLOR	MIX AB
24)	MIREX	MIX AB
25)	O, P'-DDE	MIX AB
26)	O, P'-DDD	MIX AB
27)	O, P'-DDT	MIX AB
28)	P, P'-DDE	MIX AB
29)	P, P'-DDD	MIX AB
30)	P, P'-DDT	MIX AB
31)	TOXAPHENE	INDIVIDUAL

ENVIRONMENTAL MONITORING DIVISION
HTP LABORATORY – PROCESS CONTROL LAB
STANDARD OPERATING PROCEDURE for

Total Suspended Solids Test

(SM 20TH ED. Method 2540 D)

EMD SOP#

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APPROVAL:

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1. Scope and Application

This method is applicable to water, wastewater and industrial wastes. Suspended Solids (SS) and VolatileSS (VSS) data of activated sludge is particularly useful for estimating biomass content in the wastewater aerobic treatment process. This is essential for the plant operation since it's one of the control parameters in the secondary activated sludge treatment process – directly used in loading, wasting and feeding cycles in the plant. Suspended solids also is, logically, a measure of water's cleanliness, and thus the "purity" of water. Besides BOD, pH, settleable solids, turbidity, and D.O., SS is also one of the most widely used parameters for assessing water quality and a discharger's compliance with regulatory agency requirements. In the analysis, accuracy and precision of the SS analysis in all samples is limited by the total surface area and the average pore sizes of the glass fiber filter (GFF) used. Proper sample aliquot volumes are necessary to ensure each sample yields residue in the range of 2.5 to 200 mg, captured by the GFF.

2. Summary of Method

A measured volume of well mix sample is filtered through a glass fiber filter (GFF). The solids retained on the filter are dried at $103^{o}C$-$105^{o}C$, to constant weight. For the routine samples analyzed in the laboratory, one hour drying time is sufficient. The SS is calculated as mg/L.

3. Interferences

Exclude large floating particles or submerged agglomerates of heterogeneous materials from the sample if it is determined that their inclusion is not desired in the final result (consult with client if necessary). The sample size should be limited to that which yields between 2.5 - 200 mg of residue, to prevent excessive residue on the filter that may form a water-entrapped crust or excessively decrease the average pore sizes of the GFF. Lower residue may be permitted for very clean samples with the presumed understanding that the results can yield a greater range of uncertainty.

Residues obtained from samples containing high dissolved solids, if not washed thoroughly, will include the mass of the soluble solids retained by the filter paper.

Reduce sample size, if necessary, to avoid prolonged filtration times that may cause filter clogging, producing high results caused by the increase of small or colloidal materials captured in the clogged filter.

4. Sampling and Sample Handling

Samples are collected in plastic or glass containers. No preservative is necessary but the samples should be refrigerated at all times. The recommended holding time is 7 days. Biologically active samples may be more likely to undergo changes in physical characteristics, that may be detected in the SS test, so these samples should be analyzed ASAP.

5. Apparatus

Glass Fiber Filters (GFF), Whatman 934 AH
Filtration apparatus/vacuum manifold
Laboratory vacuum pump
Vacuum flask fitted with implosion jacket
Graduated cylinders
Wide bore serological pipettes (for sludge and activated sludge samples)

Aluminum dishes (to hold GFF filters)
Drying oven, maintained at 103°C-105°C
Analytical balance, capable of weighing to 0.1 mg
Magnetic stirrer, magnetic stir bars, stirring rods
Calipers or filter pad tweezers

6. Chemicals and Reagents

Laboratory reagent grade water

7. Safety

Gloves, goggles, and protective clothing should be worn when handling samples and chemicals. Refer to MSDS sheets for toxicity of reagents and chemicals used. Good laboratory practice is enforced at all times. Wear heat insulated gloves when handling samples to and from the oven. Use rubber suction bulb, never with mouth to pipette samples.

8. Procedure

8.1 Preparation of Filters

a. Place 4.7 cm glass fiber filter (GFF, Whatman 934AH) on filter apparatus, wrinkled side up. Wash with about 20 ml distilled water. Vacuum dry.

b. Place dried filter papers in a porcelain dish and dry at 103°C oven for 1 hour.

c. Cool and store filters in desiccator, then weigh.

d. If analysis is to continue onto Volatile Total Suspended Solids, then also ignite the filters in a 550°C furnace for 15 minutes, then allow to cool then store in a desiccator, then weigh.

e. Repeat cycles of drying or igniting, cooling, desiccating, and weighing until a constant weight is obtained or until weight change is less than 4% of the previous weighing or 0.5 mg, whichever is less.

8.2 Analysis

a. Open up Sewage.xls worksheet and Record Analyst's name into worksheet. Check the balance calibration by weighing a 1.0000 g reference weight. Have weight's mass recorded into the workbook. Make corrections to any of the volumes to be used for the day, or any changes in samples within the sample set.

b. Remove the pre-washed filter from desiccator and weigh on an analytical balance to 0.1 mg. Record tare weights on the worksheet. Place in labeled aluminum dish.

c. Place GFF on filter apparatus, wrinkled side up. Apply suction. Wet with a small amount of distilled water to seat.

d. Place stir bar in sample and stir on magnetic stir plate. Mix rapidly but not excessively turbulent. (For non-routine samples: only if necessary and with the agreement of the client, have sample blended prior to this step to make it more homogeneous. Try to limit blending time to 30 seconds or less). Alternately, Shake the sample bottle thoroughly and remove the cap with lightning speed. Using a pipette, draw up the required volume (enough to produce up to 200 mg of residue) and transfer it to the GFF. Or, if a larger volume is required (>25mL), shake the sample, quickly uncap (so as to keep suspended) and pour the volume into a graduated cylinder, then pour into the filter.

e Continue suction until the liquid is gone. Wash graduated cylinder (or the pipette) onto the GFF to capture any adhering particles. Then wash residue with three (3) 10 ml portions of distilled water, allowing complete drainage between washings. Continue suction until filtration is complete.

f. Turn the vacuum off. Carefully remove GFF using forceps. Place in the pre-labeled aluminum dish and dry in a 103^{o}C oven for 1 hour. The samples routinely analyzed in the HTP-PC lab have been shown to be dried to constant weight after 1 hour in the oven. When dealing with non-routine samples, make sure samples are dried to constant weight.

g. Remove from oven and Transfer GFF to desiccator to equilibrate to balance temperature (20-30 minutes). *CAUTION: Wear heat insulated gloves!*

h. Weigh on analytical balance to 0.1 mg. For non-routine samples, dry to a constant weight of <0.4% weight loss (or 0.5 mg, whichever is less). The weight difference represents total suspended solids.

9. Calculation

Data is calculated automatically by the worksheet (an *MSExcel* spreadsheet). The following are the calculations and/or constants that the worksheet performs on the raw data input by the analyst:

$$\text{Total suspended solids (mg/L)} = \frac{(A-B)\times 1000}{Vs}$$

where: A = weight of filter + residue, mg
B = weight of filter, mg
Vs = sample volume, ml

10. Data Management

Results are sent to the LIMS database via a button on the worksheet ("Send To LIMS"), which has a macro specifying the sample's specifications (name/type, date, result, units, etc…). Worksheets for this analysis are stored with the filename syntax SW*yymmdd*.xls in the folder SEWAGE under the directory SEWAGE.

11. Quality Assurance and Quality Control

Two blanks are analyzed with each batch of samples. For every set of 10 samples, a set of duplicates is analyzed. The relative percent difference between replicates should not be greater than 10%.

12. Method Detection Limit

The MDL has been determined to be 2 mg/L.

13. Lowest Reporting Level

Has yet to be determined.

14. Precision and Bias statement

Refer to Standard Methods Edition 20, method 2540 D for statements relevant to precision & bias of the test.

15. References

Standard Methods for the Examination of Water and Wastewater, 20th Ed., 1998

16. Appendices

ENVIRONMENTAL MONITORING DIVISION
HTP LABORATORY – PROCESS CONTROL LAB
STANDARD OPERATING PROCEDURE for

Total Dissolved Solids Dried at 180°C

(SM 20th ED. 2540C)

EMD SOP # 5700

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APPROVAL:

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1. Scope and Application

This method is used in the analysis of water, wastewater, domestic and industrial wastes. The applicable range and accuracy are limited by the intrinsic residue of individual samples. Increasing accuracy and precision can be achieved by multiple drying, cooling and weighing cycles.

2. Summary of Method

A measured volume of sample is filtered through glass fiber filter. The filtrate is initially evaporated to dryness in 85° C oven and finally dried to a constant weight at 180° C. The dried residue represents the total dissolved solids (TDS).

3. Interferences

Highly mineralized waters with a considerable calcium, magnesium, chloride, and/or sulfate content may be hygroscopic and require prolonged drying, proper desiccation, and rapid weighing. Samples high in bicarbonate require careful and possibly prolonged drying at 180° C to insure complete conversion of bicarbonate to carbonate. Limit sample to no more than 200 mg residue to avoid formation of a water-trapping crust caused by excessive residue.

4. Sampling and Sample Handling

Samples are collected in plastic or glass containers. Preservation is impractical so if analysis cannot begin *ASAP*, the samples must be refrigerated and should be analyzed within 7 days.

5. Apparatus

Filtration apparatus
50 ml pipettes or graduated cylinders
Evaporating dishes
Glass fiber filter (GFF) papers
Drying oven for operation at 85°C
Desiccator
Drying oven for operation at 180°C
Analytical balance capable of weighing 0.1 mg

6. Chemicals and Reagents

None

7. Safety

Gloves, goggles, and protective clothing should be worn when handling samples and chemicals. Refer to MSDS sheets for toxicity of reagents and chemicals used. Good laboratory practice is enforced at all times.

Use caution when moving things into and out of the ovens. Use heat-resistant gloves wherever practical.

8. Procedure

8.1 Preparation of glass-fiber filter disk:

- Insert disk with wrinkled side up into filtration apparatus.
- Apply vacuum and wash disk with three successive 20-mL volumes of reagent grade water. Continue suction to remove all traces of water. Discard washings.

8.2 Preparation of evaporating dish:

- Heat clean dish to 180° C for 1 hour in an oven.
- Store in desiccator until needed.
- Weigh immediately before use.

8.3 Sample analysis:

- Use enough sample so as to leave a residue in the approximate range: 2.5 mg < Sample < 200 mg.
- Pipette a measured volume of a well-mixed sample onto a glass fiber filter with applied vacuum.
- Wash with three successive 10 ml volumes of reagent grade water, allowing complete drainage between washings. Continue suction for three minutes after filtration is complete.
- Gravimetrically transfer filtrate with washings to a weighed evaporating dish. Place in 85° C oven and allow the filtrate to evaporate to dryness (may take several hours), then transfer the dishes to the 180° C oven and continue drying for 1 hour.
- Cool the evaporating dish in a desiccator and weigh the dish immediately after taking out from the desiccator.
- Return the dishes to the 180° C oven for another hour, cool in desiccator, and reweigh. If constant weight[3] has not been obtained, then repeat the cycle until it does.

9. Calculation

Data is calculated automatically by the worksheet (an *MSExcel* spreadsheet). The following are the calculations and/or constants that the worksheet performs on the raw data input by the analyst:

[3] Constant weight is a change of ≤ 4% of previous weight or < 0.5 mg, whichever is less.

$$\text{Total dissolved solids (mg/L)} = \frac{(A-B)\times 1000}{Vs}$$

where: A = weight of dish + dried residue, mg
B = weight of dish, mg
Vs = sample volume, mL

10. Data Management

Results are sent to the LIMS database via a button on the worksheet ("Send To LIMS"), which has a macro specifying the sample's specifications (name/type, date, result, units, etc…). Worksheets for this analysis are stored with the filename syntax **Sw***yymmdd*.xls in the folder Sewage under the directory SEWAGE.

The analyst is responsible for assuring compliance with QA-QC requirements. The supervisor is notified when results are out of range. The analysis is repeated for confirmation.

11. Quality Assurance and Quality Control

A set of duplicates is analyzed for each set of 10 samples or a batch. Relative percent difference of the duplicates should not be more than 15. Also run a minimum of one blank sample using freshly distilled water in place of a sample. Residue of the blank should not exceed 5% of the sample with the lowest TDS in the batch.

12. Method Detection Limit

The MDL for this method using wastewater samples has been determined to be 32 mg/L.

13. Lowest Reporting Level

The latest TDS analysis of seven identical HTP 5-Mile effluents was done on 4/07/02. The mean of the seven replicates is 858 mg/L and the standard deviation is 10.68. With 99% confidence level, MDL of HTP 5-Mile effluent was found to be 16 mg/L.

The prior TDS analysis of seven identical HTP secondary effluents was done on 5/15/00. The mean of the seven replicates was 794 mg/L and the standard deviation was 6.87. With 99% confidence level, MDL of HTP secondary effluent was found to be 22 mg/L.

14. Precision and Bias statement

Seven tests conducted on diluted HTP effluent in 1998 yielded a mean TDS of 63 mg/L and the standard deviation of 12. Another set of seven tests with different dilution was done in 1997, gave a mean TDS of 271 mg/L with the standard deviation of 25. Method bias cannot be determined.

Refer to Standard Methods Edition 20, method 2540C for statements relevant to precision & bias of the test.

15. References

Standard Methods for the Examination of Water and Wastewater, 20th Ed., 1998

16. Appendices

None

ENVIRONMENTAL MONITORING DIVISION
HTP LABORATORY – PROCESS CONTROL LAB
STANDARD OPERATING PROCEDURE for

SETTLEABLE SOLIDS ANALYSIS

(SM 20TH ED. 2540 F)

EMD SOP# 5600

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APPROVAL:

Laboratory Manager: Dr. Farhana Mohamed
Signature: _____

Quality Assurance Manager: Dr. Sumitra Roy-Burman
Signature: _____

Quality Assurance Officer: Dr. Mahesh Pujari
Signature: _____

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1. Scope and Application

This method is used in the analysis of water and wastewater. Settleable solids data together with total suspended solids, floatable solids, and turbidity data would provide a much better assessment of the over all physical quality of water sample than any stand alone datum will. Determination of settleable solids of primary clarifier effluent is essential for the optimization of the primary and secondary treatment processes in a wastewater treatment plant. Settleable solids of effluent is often used by regulators to gauge the physical quality of the treated discharge water.

2. Summary of Method

Volumetric: A liter of sample is allowed to settle in an Imhoff cone for 1 hour and the volume of the settled solids measured. The solids represent the settleable solids of the sample.

3. Interferences

If the settled matter contains pockets of liquid between large settled particles, estimate volume of pockets and subtract from volume of settled solids.

Where there is a separation of floating materials from the settleable solids, do not estimate the floating material as settleable matter.

4. Sampling and Sample Handling

Samples are collected in 1 liter plastic or glass containers. No preservative is required but if not analyzed immediately, the samples need to be refrigerated ASAP and must be analyzed within 7 days. For samples that contain biological floc that may change its characteristic with time, run the analysis ASAP.

5. Apparatus

Imhoff cones Timing device, for 15 minute increments and 1 hour.
Support rings or rack for imhoff cones Long (20”), straight, narrow (2mm) wire

6. Chemicals and Reagents

None.

7. Safety

Gloves, goggles, and protective clothing should be worn when handling samples and chemicals. Refer to MSDS sheets for toxicity of reagents and chemicals used. Good laboratory practice is enforced at all times.

8. Procedure

8.1 Fill an Imhoff cone with a well mixed sample to the 1L mark. Set the timer for 45 minutes.

8.2 Allow to settle undisturbed in that time frame.

8.3 After 45 minutes, gently slide the wire down inside the cone alongside the edge of the glass, and moving slowly around the circumference, scrape the inside wall of the cone to free any adhering solids, at the same time causing no turbulence that would disturb the already settled material or the body of water as a whole (no whorl turbulence). Carefully remove wire by sliding up along inside of cone. Alternately, spin (turn) the cone gently to knock adhering solids off the inside wall.

8.4 Set the timer again, this time letting it settle for 15 minutes.

8.5 At 1 hour (total time), record volume of solids and report as mL/L.

9. Calculation

There is no calculation involved. The reading, or data, is entered directly into the SEWAGE worksheet (an *MSExcel* spreadsheet) as well as the daily sample logbook.

10. Data Management

Results are sent to the LIMS database via a button on the SEWAGE worksheet ("Send To LIMS"), which has a macro specifying the sample's specifications (name/type, date, result, units, etc…). Worksheets for this analysis are stored with the filename syntax SW*yymmdd*.xls in the folder SEWAGE under the directory SEWAGE.

11. Quality Assurance and Quality Control

11.1 Standard reference material for the determination of settleable solid has been tested in 2002 by Hyperion PC laboratory for the purpose of test certification, of which passing results were achieved. A reference standard sample of settleable solids has been purchased thru Environmental Resource Associates. Test results were within acceptable ranges for that sample. See file in laboratory for more information. The solids of this check reference must be within 75 to 125 % of the assigned value.

11.2 The relative percent difference between replicates should not be greater than 20 % for samples containing 1ml/L or greater value of settleable solids.

14. Method Detection Limit

The MDL for settleable solids is 0.1 ml/L for HTP effluent.

15. Lowest Reporting Level

For wastewater, the lowest reporting level is 0.1 mL/L

14. Precision and Bias statement

Refer to Standard Methods Edition 20, method 2540F for statements relevant to precision & bias of the test.

15. References

Standard Methods for the Examination of Water and Wastewater, 20th Ed., 1998

16. Appendices

SEDIMENT QUALITY MONITORING SOPs

City of Los Angeles
ENVIRONMENTAL MONITORING DIVISION
Instrumental Chemistry Strategic Business Unit – Metals Laboratory
STANDARD OPERATING PROCEDURE for

INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRIC METHOD FOR TRACE ELEMENT ANALYSIS OF WATER AND WASTES

(EPA Methods 6010) EMD SOP# 6601.0
Effective Date: 03/23/06
Version No.: 1.2
Total Number of pages: 13
Pages Revised:

APPROVAL:
Laboratory Manager: Lee Huang
Signature:
Quality Assurance Officer: Mahesh Pujari
Signature:
Quality Assurance Manager Sumitra Roy-Burman
Signature:

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1.0 SCOPE AND APPLICATION

1.1 .Inductively coupled plasma-atomic emission spectrometry (ICP-AES) determines trace elements, including metals, in solution. The method is used in the analysis of dissolved metals in ground water and aqueous samples that are prefiltered with 0.45 um pore membrane filter and acidified to match the acid matrix of the calibration standards. It is also used in the analysis of soluble metals in TCLP and EP extracts, and the total metals in the ground water, aqueous samples, industrial wastes, suspended solids, soils, sludges, tissues and other solid wastes which have been solubilized or digested using appropriate sample preparation methods.

1.2 This method is currently used in the determination of the following analytes: aluminum, antimony. arsenic, barium, beryllium, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, molybdenum, nickel, potassium, selenium, silica, silver, sodium, strontium, thallium, tin, vanadium, and zinc.

2.0 SUMMARY OF THE METHODS

2.1 This method describes multi-elemental determination by ICP-AES using simultaneous optical system and axial viewing of the plasma. Sample is nebulized and the resulting aerosol is transported to the plasma torch. Element–specific emission spectra are produced by a radio frequency (RF) inductively coupled plasma. The spectra are dispersed by a grating spectrometer and the intensity of the emission lines are monitored by photosensitive devices. Concentration of the analyte of interest is obtained by substituting the intensity of the specific characteristic emission line in a concentration-intensity calibration curve created from the same measurement for a set of calibration standard solutions. Background correction is required for trace element determination. Background correction due to spectral interference is done by a computer inter-element correction routine.

2.2 The wavelengths listed in Table 1 are recommended for these analytes in clean aqueous matrices. Wavelengths other than those recommended may be substituted if they provide the needed sensitivity and are properly corrected for inter-element spectral interferences.

3.0 INTERFERENCE

3.1 *Spectral interferences* are caused by background emission from continuous or recombination phenomena, stray light from the emission of high concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra. Background emission and stray light are usually be compensated for by subtracting the background emission determined by measurements adjacent to the analyte wavelength peak. Spectral overlaps may be avoided by using an alternate wavelength or can be compensated by equations that

correct for inter-element contributions. Varian Vista-Pro is equipped with sophisticated software that takes care of this correction.

3.2 *Physical interferences* are effects associated with the sample nebulization and transport processes. Change in viscosity and surface tension can cause significant inaccuracy. Solution with higher total dissolved solids (TDS) than 2 % may clog or restrict the flow at the nebulizer and torch injector orifices. Physical interferences could be reduced by dilution and by using peristaltic pump in the sample delivery system.

3.3 *Chemical interferences* include molecular compound formation, ionization effects, and solute vaporization effects. Chemical interferences can be minimized by careful selection of operating conditions (RF power, nebulizer flow…), by matrix matching and by standard addition procedures.

3.4 *Memory interferences* result when analytes in a previous sample contribute to the signals measured in a new sample. Suitable rinse time should be used to minimize the memory interferences.

4.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

4.1 For the determination of dissolved elements, the sample must be filtered through a 0.45 um pore membrane filter as soon as possible or upon receipt at the lab. The filter flask is rinsed with a small portion of the filtrate before collecting the desired volume. The filtrate is then acidified immediately to pH<2. If precipitation occurs upon acidification, the sample must be dissolved again using appropriate digestion technique before starting the analysis.

4.2 For the determination of total recoverable elements in aqueous samples, the sample must be acidified to pH<2 at the time of collection. The sample should not be filtered prior to analysis. Samples that cannot be preserved at the time of collection because of sampling limitations or transport restrictions should be acidified with nitric acid to pH < 2 upon receipt in the laboratory. Following acidification, the sample should be held for 24 hours before withdrawing an aliquot for sample processing. No preservation is required for solid samples prior to analysis other than storage at 4° C. Sample holding time, digestion volumes and suggested collection volumes are listed in Table 2. The sample volumes required depend upon the number of different digestion procedures necessary for analysis. In all cases for waste testing, representative sampling must be maintained.

4.3 In the determination of trace metals, containers can introduce either positive or negative errors in the measurement of trace metals by (a) contributing contaminants through leaching or surface desorption, and (b) depleting concentrations through adsorption. Thus the collection and treatment of the sample prior to analysis require particular attention. The following cleaning treatment sequence has been determined to be adequate to minimize contamination in sample bottle, whether

borosilicate glass, linear polyethylene, polypropylene, or Teflon: detergent, tap water, 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water, and reagent water. Chromic acid should not be used to clean glassware, especially if chromium is to be included in the analytical scheme.

5.0 APPARATUS

5.1 Analytical instrumentation and supplies

5.1.1 Varian Vista-Pro inductively coupled plasma-atomic emission spectrometer

5.1.2 Dell personal computer

5.1.3 Varian autosampler

5.1.4 Varian recirculator

5.1.5 Varian variable speed peristaltic pump

5.1.6 Argon gas, liquid supply, high purity grade (99.99%), local supplier

6.0 CHEMICALS AND REAGENTS

6.1 Reagents may contain elemental impurities that might affect analytical data. Only high-purity reagents should be used whenever possible. All acids used for this method must be of ultra high purity grade. Suitable acids are available from most major suppliers.

6.1.1 Nitric acid, concentrated, trace metal grade

6.1.2 Hydrochloric acid, concentrated, trace metal grade

6.2 *Reagent Water*. For all sample preparation and dilutions, ASTM type I water is required. Suitable water is prepared by passing potable water through a mixed bed of anion and cation exchange resins. The water purifying system used at EMD labs is commercially maintained. The de-ionized water is available throughout the EMD laboratory in distinctly white faucets.

6.3 *Standard stock solutions*

6.3.1 WW-IPC-1 (Supplier: Inorganic Ventures): 1000 mg/L each P,K ; 200 mg/L each Al, As, Ba, Be, B, Cd, Ca, Ce, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Hg, Ni, Se, Na, Sr, Tl, Ti, V, Zn; 25 mg/L Ag.

6.3.2 WW-IPC-2 (Supplier: Inorganic Ventures): 1000 mg/L SiO2; 200 mg/L each Sb, Mo, Sn, Ti.

6.3.3 ICM-240 (Supplier: Ultra Scientific): 100 mg/L P, K, Si; 20 mg/L each Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Mo, Hg, Ni, Se, Na, Sr, Tl, Sn,V, Zn; 5 mg/L Ag.

6.3.4 IQC-026 (Supplier: Ultra Scientific): 1000 mg/L K; 100 mg/L each Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, Se, Ag, Na, Tl, V, Zn; 50 mg/L Si.

6.3.5 Al, Ca, Fe, Mg, K, Na (Supplier:Spex-CertiPrep): 1000 mg/L each in separate pack.

6.4 *Mixed calibration standard solutions*. A mixed calibration standard solution is prepared by combining appropriate volumes of the stock standard solutions into volumetric flasks. Concentrated nitric acid is added first to a small volume of water in the flask so that the final concentration of nitric acid will be 5%. The required volume of stock standard is added to the flask and finally diluted to volume with de-ionized water. The freshly prepared mixed calibration solution is transferred a to clean polyethylene bottle for storage. Fresh mixed calibration solutions should be prepared as needed with the realization that concentrations can change on aging. Below are the typical concentrations for the set of mixed calibration standards used at EMD lab at HTP:

6.4.1 Combined WW-IPC-1 and WW-IPC-2

6.4.2 Std.#1: 0.002 mg/L - for ML of Be only

6.4.3 Std.#2: 0.005 mg/L - for ML of Pb only

6.4.4 Std.#3: 0.010 mg/L

6.4.5 Std.#4: 0.200 mg/L

6.4.6 Std.#5: 1.000 mg/L

6.4.7 Std.#6: 2.000 mg/L

6.4.8 Std.#7: 4.000 mg/L

6.4.9 Std.#8: Combined Al, Ca, Fe, Mg, K, Na 20 mg/L

6.4.10 Std.#9: Combined Al, Ca, Fe, Mg, K, Na 40 mg/L

6.5 Blanks. Two types of blanks are required for this method. The calibration blank is used to establish the analytical calibration curve, and the laboratory method blank is used to identify possible contamination from the sample preparation procedure.

6.5.1 The *calibration blank* is prepared by acidifying reagent water to the same concentration of the acids in the standard solutions. Sufficient quantity is prepared to flush the system between samples. The calibration blank is also used for initial and continuing calibration blank determinations.

6.5.2 The *method blank* is processed in the same way as the samples and therefore should contain the same volume of reagents used. The final solution should contain the same acid concentration as the sample solutions for analysis.

6.6 The *Initial Calibration Verification* (ICV) is prepared from stock standard source different from that of the calibration standards and at concentration within the linear working range of the instrument. At EMD lab, ICV is 2.00 mg/L ICM 240.

6.7 The *Continuing Calibration Verification* (CCV) is prepared from the same stock standards that are used for the preparation of calibration standards and at concentration near the midpoint of the calibration curve. At EMD lab, CCV for low concentration analytes is 2.00 mg/L WW IPC1+2 and for high concentration analytes, CCV is 20.0 mg/L. of combined Al, Ca, Fe, Mg, K and Na.

6.8 The *Interference Check Solution* (ICS) is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. At EMD lab, ICS is prepared to contain 2.00 mg/L of WW IPC1+2 and 50 mg/L of combined Al, Ca, Fe, Mg, K and Na.

7.0 SAFETY

7.1 The toxicity and carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Specifically, concentrated HNO_3 and HCl present various hazards and are moderately toxic and extremely irritating to skin and mucus membranes. Use these reagents in a fume hood whenever possible. If eye or skin contact occurs, flush with large volumes of water.

7.2 Safety goggle and protective lab coat must be worn all the time while working in the lab. Appropriate type of gloves must be worn when handling samples and chemicals.

8.0 PROCEDURE

8.1 Sample Preparation

Preliminary treatment of most matrices is necessary because of the complexity and variability of sample matrices. Groundwater samples that have been prefiltered and acidified will not need acid digestion. Samples that are not digested must either use an internal standard or be matrix matched with the standards. Refer to methods EPA 3005A, EPA 3010A, EPA3050B and SM 3030F for the appropriate digestion procedures.

8.2 Instrument start-up and warm-up procedures:

8.2.1 Check the argon supply; turn on water chiller (temperature: <18 °C); check overhead hood.
8.2.2 Before connecting the tubings of the peristaltic pump, inspect for wear and tear.
8.2.3 Clean the optical plasma interface (OPI) to avoid problem with ignition of plasma.
8.2.4 Refill reservoir with calibration blank to flush the system.

8.2.5 For Varian Vista-Pro: In the ICP Expert software, click ”Instrument” to display the instrument parameters on the screen.
8.2.6 Purging, ignition of plasma and pump control are activated by clicking “Plasma on” icon.
8.2.7 After lighting the plasma, wait for at least 30 minutes before starting analysis.

Optimization of the instrument

8.3.1 The plasma operating conditions need to be optimized prior to use of the instrument. This is required only when first setting up a new instrument or following a change in operating conditions. The purpose of plasma optimization is to provide a maximum signal to background ratio for some of the least sensitive elements in the analytical array. Check the plasma and sample introduction system by running a solution of yttrium. Care must be taken so that the sample penetrates the plasma and the channel appears in the plasma. While aspirating the yttrium solution, the aerosol carrier gas can be adjusted so a definitive blue emission region of the plasma extends approximately from 5 to 20 mm above the top of the load coil. The yttrium solution can also be used for coarse alignment of the torch by observing the overlay of the blue light over the entrance slit to the optical system. If either operating conditions, such as incident power or nebulizer gas flow rate are changed, or a new torch is installed, the plasma should be re-optimized.

8.3.2 Varian ICP Expert software has the capability for automated torch alignment and optimization. With the sample pump inlet tube placed in a 5 ppm Mn solution, click “Torch Align” from the Instrument Setup window. The Torch

Alignment file consists of a single line, Mn 257.610 nm, that is recommended because it gives a representative viewing range scan for most elements. Click "Torch Scan" on the Torch Align page to perform horizontal and vertical scans. When the instrument scans the torch, it will move the pre-optics to the optimum positions for viewing the plasma.

Calibration and Analysis

From the Worksheet window, click "new", and enter the filename "yyyymmdd". Select the method to be used from the list of methods then save the file. Click "Sequence", then "Sequence editor" and enter the total number of samples (including QC check samples). The samples names are listed in the order desired. To start calibration and analysis, first highlight the standards and samples then click on the lighted green arrow. The Varian ICP Expert software has the capability to mask each individual result and replicate and to edit calibration and base line correction. By carrying out such editing, time can be saved in not having to re-run a particular standard or sample. It also allows the analyst to export only the data of the desired elements for further data reduction or reporting.

8.5 MDL and RDL

8.5.1 Method detection limits must be established for all wavelengths utilized for each type of matrix commonly analyzed. The matrix used for the MDL calculation must contain analytes of known concentrations within 3-5 times the anticipated detection limits. Refer to 40 CFR Vol. 68, appendix B to part 136 " Definition and Procedure for the Determination of the Method Detection Limits – Revision 2" for guidance for the MDL determination. One must recognize that determination of limits using reagent water represent a best-case situation and do not represent possible matrix effects of real world samples.

8.5.2 The upper limit of the linear dynamic range must be established for each wavelength utilized by determining the signal responses from a minimum of three, preferably five, different concentration standards across the range. One of these should be near the upper limit of the range. The range to be used for the analysis of sample should be judged by the analyst from the resulting data. The data, calculations and rationale for the choice of range made should be documented and kept on file. The upper range limit shall be an observed signal no more than 10 % below the level extrapolated from lower standards.

8.5.3 Determined analyte concentrations that are above the upper range limit must be diluted and reanalyzed.

8.5.4 It should be noted that linear response curves must be used for all elements. At least three standards and a blank must be used for least squares linear

calibration fitting (see 15.0) and the correlation coefficient must be 0.995 or greater .

9.0 CALCULATION

9.1 If a dilution factor is entered into the method, the ICP Expert software will calculate and print the corrected concentration. If a weight to volume factor is used it would also correct the analyzed data for this factor.

10.0 DATA MANAGEMENT

10.1 Raw data in VWS format that are generated from the Varian ICP-Expert software are stored in ICP computer hard drive and in EMDB\ icp_rawfiles\yyyy. The extracted data file, including calculated QC and spike % recoveries that are generated from an excel template developed for the lab are saved in the subdirectory EMDB\icp_data\yyyy. Approved data are entered in LIMS.

11.0 QUALITY ASSURANCE AND QUALITY CONTROL

11.1 A minimum of one *method blank* per sample batch is required to determine if contamination or any memory effects are occurring.

11.2 A *matrix spiked duplicate sample* is analyzed at a frequency of one per matrix batch. The spike recovery should be within 25% of the actual value or within the documented historical acceptance limits for each matrix. It is recommend that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests are: a) Dilution test; if the analyte concentration is sufficiently high (minimally, a factor of 10 above the IDL after the dilution), an analysis of 1:5 dilution should agree within ± 10% of the original determination. If not, a chemical or physical interference effect should be suspected. b) Post Digestion Spike Addition; an analyte spike added to a portion of a prepared sample, or its dilution, should be recovered within 75% to 125% of the known value. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the IDL. If the spike is not recovered within the specified limits, a matrix effect should be suspected. A control limit of 20% RPD or within the documented historical acceptance limits for each matrix should be used for sample values greater than ten times the IDL.

11.3 Instrument standardization is checked by analyzing appropriate QC samples:

11.3.1 A *calibration blank* is run immediately following daily calibration, after every ten samples, and at the end of an analytical run. The results of the calibration blank should agree within three times the IDL. If the limit is exceeded, the analysis is repeated two more times and the average of the results taken. If the average is not within three standard deviations of the

background mean, the analysis is terminated, the problem is corrected, and the instrument is recalibrated.

11.3.2 *Initial Calibration Verification* (ICV, 2 ppm ICM 240 sol.) standard is run following initial calibration. The results should agree within 10% of the expected value with relative standard deviation of three replicates smaller than 5%. If the limit is exceeded, the analysis is terminated, the problem is corrected and the instrument is recalibrated.

11.3.3 The *Continuing Calibration Verification* (CCV, 2 ppm WW-IPC1 + WWIPC2 sol.) standard is analyzed immediately following daily calibration, every ten samples and at the end of the analytical run. The results should agree within 10% of the expected value with relative standard deviation of three replicates smaller than 5%. If the limit is exceeded, the analysis is terminated, the problem is corrected and the instrument is recalibrated.

11.3.4 *Interference Check Solution* (ICS) is analyzed at the beginning of each run to verify the inter-element and background correction factors. The results must be within 20% of the true value.

11.4 Documentation. Analysts are required to sign in on ICP Login/Maintenance binder in Room 507 every time the instrument is used and to record any problem encountered during the analysis. All routine maintenance and repair done by the vendor/manufacturer are kept in a separate section of the ICP Login/Maintenance binder.

11.5 Records. All raw data shall be maintained either in the laboratory facility or in a suitable storage location for a period of not less than 3 years or since the last on-site audit of the Environmental Laboratory Accreditation Program, whichever is longer.

12.0 LOWEST REPORTING LEVEL

12.1 ML and MDL for metals by EMD lab at HTP are listed in EMDB/MDL/2003/ML-MDL-DI WATER-ICP VARIAN 2003.XLS file.

12.2 Report data in mg/L up to three significant figures. Round the concentration value to the thousandth place. Concentration values equal or greater than the ML are reported as is. Concentrations equal or greater than the MDLs, but lower than the MLs report the values as an estimate values. Concentrations lower than the MDLs are reported as ND.

13.0 PRECISION AND BIAS STATEMENT

13.1 Control charts for precision and accuracy are updated periodically for review.

13.2 Internal quality control sample, provided by EMD Quality Assurance Unit, is analyzed frequently for accuracy check.

13.3 A performance evaluation study of trace metals is done annually as part of the requirement of Environmental Laboratory Accreditation Program.

14.0 REFERENCES

1. EPA method 6010B, revision 2, December 1996.

2. SW-846 Third edition,1998.

3. SM 3120B, Metals By Plasma Emission Spectroscopy, Standard Method For The Examination Of Water and Wastewater, 20th. Edition, 1998.

15.0 LEAST SQUARES FIT.

The determination of a functional relationship between measured intensities of a line and given concentrations of an element emitting the line is called calibration. The calibration function is determined by performing a certain number of measurements of standards having a known concentration of the element (data points). Least squares fitting, used to adjust the calibration curve to these data points, is done by minimizing the sum of the squared differences between the calculated and the certified concentrations:

$$X^2 = \Sigma (\omega_i (C_{i, cert} - C_{i, Calc}))^2$$

The ω_i are the weighting factors.

The parameters of the calibration curve, obtained from the condition for a minimum of X^2, may be calculated by the Varian software.

TABLE 1: RECOMMENDED WAVELENGTHS

Analyte	Wavelength (nm)
Aluminum	308.215
Antimony	206.833
Arsenic	193.759
Barium	493.409
Beryllium	313.042
Boron	249.678
Cadmium	226.502
Calcium	315.887
Cerium	413.765
Chromium	205.552
Cobalt	228.616
Copper	324.754
Iron	259.940
Lead	220.353
Lithium	670.784
Magnesium	279.079
Manganese	257.610
Mercury	194.227
Molybdenum	203.844
Nickel	231.604
Phosphorus	214.914
Potassium	766.491
Selenium	196.090
Silica (SiO2)	251.611
Silver	328.068
Sodium	588.995
Strontium	421.552
Thallium	190.864
Tin	189.980
Titanium	334.941
Vanadium	292.402
Zinc	213.856

The wavelengths listed are recommended because of their sensitivity and overall acceptability. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference.

TABLE 2

SAMPLE HOLDING TIMES, RECOMMENDED DIGESTION VOLUMES AND RECOMMENDED COLLECTION VOLUMES FOR INORGANIC DETERMINATION IN AQUEOUS AND SOLID SAMPLES.

Measurement		Digestion Volume(ml) a,c	Collection Volume(ml)a,c	Treatment/Preservative Holding Time b
Inorganic Analytes				
Aqueous				
	Total	100	600	HNO_3 to pH<2 6 months
	Dissolved	100	600	Filter on site HNO_3 to pH<2 6 months
	Suspended	100	600	Filter on site 6 months
Solid				
	Total	2 g	200 g	6 months

a Unless stated otherwise
b Either glass or plastic containers may be used.
c Any sample volume reduction from the reference method's instructions must be made in the exact proportion as described in the method and representative sampling must be maintained.

City of Los Angeles
ENVIRONMENTAL MONITORING DIVISION
Instrumental Chemistry Strategic Business Unit
Semi – Volatile Organic Laboratory
STANDARD OPERATING PROCEDURE for

Semivolatile Organic compounds by Gas Chromatography/Mass Spectrometry

(EPA Method 8270C) SOP# IC-BNA-02

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APPROVAL:

Laboratory Manager: Lee Huang
Signature: _____

Quality Assurance Officer Mahesh Pujari
Signature: _____

Quality Assurance Manager: Jeffrey Beller
Signature: _____

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1. SCOPE AND APPLICATION

1.1. This method covers the determination of a number of organic compounds that are partitioned into an organic solvent and are amenable to gas chromatography. The parameters listed in Tables 1 and 2 may be qualitatively and quantitatively determined using this method.

1.2. The method may be extended to include the parameters listed in Table 3. Benzidine can be subject to oxidative losses during solvent concentration. Hexachlorocyclo-pentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition. N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described. N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine.

1.3. This is a gas chromatographic/mass spectrometry (GC/MS) method applicable to [2,10] the determination of the compounds listed in Tables 1, 2, and 3 in extracts prepared from many types of solid waste matrices, soils, air sampling media and water samples.

1.4. The method detection limit (MDL, defined in Section 16.1) [1] for each parameter is listed in Tables 5. The MDL for a specific sample type may differ from those listed, depending upon the nature of interferences in the sample matrix.

1.5. This method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph/mass spectrometer and in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.

2. SUMMARY OF METHOD

2.1. This method describes the quantitative determination of semivolatile organic compounds using GC/MS. Most neutral, acidic and basic organic compounds that are soluble in

methylene chloride and capable of being eluted as sharp peaks from gas chromatographic fused silica capillary column coated with slightly polar silicone can be determined by this method.

2.2. The following compounds may require special treatment when being determined by this method. Benzidine can be subject to oxidative loss during solvent concentration. Also Chromatography is poor. Hexachlorocyclopentdiene is subject to thermal decomposition. N-nitrosodiphenylamine co elutes with diphenylamine. Most substituted phenols, nitroanilines, benzoic acid and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling point material.

2.3. Soil samples must first be extracted at a neutral pH by Accelerated Solvent Extraction (ASE). Water samples must be extracted using either continuous extraction or separatory funnel shakeout. The final volume of the extract is brought to 1 mL.

2.4. Qualitative identification of target analytes is achieved by comparing mass spectra and relative retention time of standards.

2.5. Target analyte concentration is then determined by the use of internal standards. Extraction efficiency is determined by surrogate's recoveries and recoveries of laboratory control sample (LCS).

3. INTERFERENCES

3.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the total ion current profiles. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.1.3.

3.1.1. Glassware must be scrupulously cleaned.[3] Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Solvent rinsing should be followed by detergent washing with hot

water, and rinses with tap water and distilled water. The glassware should then be drained dry, and rinsed with acetone and pesticide quality hexane. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.1.2. The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.2. Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled.

3.3. The base-neutral extraction may cause significantly reduced recovery of phenol, 2-methylphenol, and 2,4-dimethylphenol. The analyst must recognize that results obtained under these conditions are minimum concentrations.

4. SAMPLE COLLECTION, PRESERVATION AND HANDLING

4.1. Sample Bottles and Jars.

4.1.1. Samples are collected in glass bottles or jars with Teflon-lined caps. Plastic bottles must not be used since they are known to introduce interferences and absorb pesticides.

4.1.2. The glass bottles or jars are pre-washed with liquid detergent, hot tap water, distilled water, and followed by rinsing with hexane.

4.2. Grab samples must be collected in glass containers. Conventional sampling practices[7] should be followed, except that the bottle must not be pre-rinsed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be as free as possible of Tygon tubing and other potential sources of contamination.

4.3. All samples must be iced or refrigerated at 4°C from the time of collection until extraction.

4.4. Sample receiving: All samples are received and logged into LIMS by Data and Sample Management (DSM) SBU at the Central Receiving Area. When preparation and analysis are needed, samples will be checked out from Central Storage Rooms. After the required volume of samples is taken, samples will be returned to Central Receiving Area for further storage.

4.5. Registering the sample: Samples received in the laboratory are registered in the sample log book where each sample is assigned a unique "sample number" (e.g. Sample Number P-6-3-025; such as P for plant samples, 6 for year 1996, 3 for month March, 025 for sequential number, type of analysis required are assigned by letters; P for pesticides, BNA for Base/Neutral Acids, and V for volatiles. The LIMS login number assigned to each sample by DSM is also recorded in the laboratory log book.

4.6. Sample storage and holding time

4.6.1. Samples are to be stored in a refrigerator at 4 °C.

4.6.2. Extractions for BNA must be performed within 7 days of sample collection for liquid samples, 14 days for solid samples and 6 months for frozen solid samples.

4.6.3. Extracts must be analyzed within 40 days of the extraction date.

5. APPARATUS

5.1. Sampling equipment, for discrete or composite sampling.

5.1.1. Grab sample bottle—1 L, amber glass, fitted with a screw cap lined with Teflon. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The bottle and cap liner must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

5.1.2. Automatic sampler (optional)—The sampler must incorporate glass sample containers for the collection of a minimum of 250 mL of sample. Sample containers must be kept refrigerated at 4°C and protected from light during compositing. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used. Before use, however, the compressible tubing should be thoroughly rinsed with methanol, followed by repeated rinsing with distilled water to minimize the potential for contamination

of the sample. An integrating flow meter is required to collect flow proportional composites.

5.2. Glassware

5.2.1. Separatory funnel—2 L, with Teflon stopcock.

5.2.2. Funnels and glass wool

5.2.3. Concentrator tube, Kuderna-Danish—10 mL, graduated. Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

5.2.4. Evaporative flask, Kuderna-Danish—500 mL. Attach to concentrator tube with springs.

5.2.5. Snyder column, Kuderna-Danish—Three balls.

5.2.6. Vials—1 mL, 10-15 mL, amber glass, with Teflon-lined screw cap.

5.2.7. Continuous liquid-liquid extractor, 250-mL round-bottom flask and condenser — Equipped with Teflon or glass connecting joints and stopcocks requiring no lubrication.

5.3. Heating mantel, temperature controller, and timer.

5.4. Various kinds of gas tight syringes (10 µl, 25 µl, 50 µl, 100 µl, 1000 µl).

5.5. Zymark TurboVap 500 Concentrator, capable of temperature control (2°C).

5.6. VWR Circulating Cooling System.

5.7. Boiling chips—Approximately 10/40 mesh. Heat to 400°C for 30 minutes of Soxhlet extract with methylene chloride.

5.8. Water bath—Heated, with concentric ring cover, capable of temperature control (2°C). The bath should be used in a hood.

5.9. Balance—Analytical, capable of accurately weighing 0.0001 g.

5.10. GC/MS system

5.10.1. Gas Chromatograph—An analytical system complete with a temperature programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases.

5.10.2. Column—30-m x 0.25-mm I.D. 0.25-μm film thickness silicon-coated fused-silica capillary column (J&W Scientific DB-5).

5.10.3. Mass spectrometer—Capable of scanning from 35-450 amu every seven seconds or less, utilizing a 70 V (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all the criteria in Table 9 when 50 ng of decafluorotriphenyl phosphine (DFTPP; bis (perfluorophenyl) phenyl phosphine) is injected through the GC inlet.

5.10.4. GC/MS interface—Any GC to MS interface that gives acceptable calibration points at 50 ng per injection for each of the parameters of interest and achieves all acceptable performance criteria (Section 8.3.2) may be used. GC to MS interfaces constructed of all glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

5.10.5. Data system—A computer system must be interfaced to the mass spectrometer, which is capable of continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for specific m/z and plotting such m/z abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time and scan number limits.

5.10.6. Three HP GC/MSD with HP-ChemStation GCMS software and HP 7673 Autosampler are used:

	Instrument Name	Instrument Model	Injection Type
BNA #1	**HP 5890 GC/ 5972 MSD**		**Split/Splitless**
	BNA #2	HP 5890 GC/ 5972 MSD	Cool-on-Column
	BNA #3	HP 6890 GC/ 5973 MSD	Split/Splitless

6. CHEMICALS AND REAGENTS

6.1. Reagent water—Reagent water is defined as water in which an interferent is not observed at the MDL of the parameters of interest.

6.2. Sodium hydroxide solution (10 N)—Dissolve 40 g of NaOH (ACS) in reagent water and dilute to 100 mL.

6.3. Sodium thiosulfate—(ACS) Granular.

6.4. Sulfuric acid (1+1)—Slowly, add 50 mL of H_2SO_4 (ACS, sp. gr. 1.84) to 50 mL of reagent water.

6.5. Acetone, methanol, hexane and methylene chloride—Pesticide quality or equivalent.

6.6. Sodium sulfate—(ACS) Granular, anhydrous. Purify by heating at 400°C for four hours in a shallow tray.

6.7. Stock standard solutions—standard solutions are purchased from Supelco.

6.7.1. Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

6.7.2. Stock standard solutions must be replaced after six months, or sooner if comparison with quality control check samples indicates a problem.

6.7.3. When the working standards are prepared from the stock standards, pertinent information are documented in the standards logbook for BNA.

6.7.4. Following standards are used, 2000 µg/mL each:

Base/Neutrals Mix (cat # 4-7991)

Polynuclear Aromatic Hydrocarbons Mix (cat # 4S8905)

Phenols Mix (cat # 4S8904)

Benzidines Mix (cat # 4S8906)

Hardazdous Substances Mix (cat # 4-7990)

6.8. Surrogate standard spiking solution— Surrogate standards consisting of six surrogate compounds are purchased from Supelco. Store the spiking solution at 4°C in Teflon-sealed glass container. The solution should be checked frequently for stability. The solution must be replaced after six months, or sooner if

comparison with quality control checks standards indicates a problem.

6.8.1. Surrogate standards, 4000 µg/mL, Purchased from Supelco, contains 3 BN and 3 acid surrogates (cat # 4-7960):

Phenol-d6	Nitrobenzene-d5
2-Fluorophenol	2-Fluorobiphenyl
2,4,6-Tribromophenol	p-Terphenyl-d14

6.9. Internal standard solution— Internal standards consisting of six compounds are purchased from Supelco. Store the spiking solution at 4°C in Teflon-sealed glass container. The solution should be checked frequently for stability. The solution must be replaced after six months, or sooner if comparison with quality control checks standards indicates a problem.

6.9.1. Internal standards, 2000 µg/mL each in methylene chloride, Purchased from Supelco, contains 6 compounds (cat # 4-8902):

Acenapththene - d10	Naphthalene - d8
Chrysene - d12	Perylene - d12
1,4-Dichlorobenzene - d4	Phenanthrene - d10

6.10. DFTPP standard— DFTPP standard is purchased from Supelco. Prepare a 50 µg/mL solution of DFTPP from the 2000 µg/mL concentrate.

6.11. Quality control check sample concentrate— Secondary source standard solutions are purchased from Ultra Scientific.

7. SAFETY

7.1. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified for the information of the analyst. [4-6]

7.2. The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzo(a)anthracene, benzidine, 3,3'-dichlorobenzidine, benzo(a)pyrene, dibenzo(a,h)anthracene, and N-nitrosodimethylamine. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

8. PROCEDURE

8.1. Separatory Funnel Extraction

8.1.1. Samples can be extracted either using separatory funnel technique or continuous extraction (Section 8.2) technique. The separatory funnel extraction scheme described below assumes a sample volume of 1 L.

8.1.2. Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2 L separatory funnel. Add the surrogate standard spiking solution into the separatory funnel and mix well. Check the pH of the sample with wide-range pH paper and adjust to pH >11 with sodium hydroxide solution.

8.1.3. Add 50 mL of methylene chloride to the sample bottle, seal, and shake for 30 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for two minutes with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 250 mL Erlenmeyer flask.

8.1.4. Add a second 50 mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner. Label the combined extract as the base/neutral fraction.

8.1.5. Adjust the pH of the aqueous phase to less than 2 using sulfuric acid. Serially extract the acidified aqueous phase three times with 50

mL aliquots of methylene chloride. Collect and combine the extracts in a 250 mL Erlenmeyer flask and label the combined extracts as the acid fraction.

8.1.6. For each fraction, assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 mL concentrator tube to a 500-mL evaporative flask.

8.1.7. For each fraction, pour the combined extract through a solvent-rinsed funnel containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and funnel with 20-30 mL of methylene chloride to complete the quantitative transfer.

8.1.8. Add one or two clean boiling chips and attach a three-ball Snyder column to the evaporative flask for each fraction. Pre-wet each Snyder column by adding about 1 mL of methylene chloride to the top. Place the K-D apparatus on a hot water bath (60-65°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-20 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of methylene chloride. A 5 mL syringe is recommended for this operation.

8.1.9. Combine the acid extract evaporated to about 5 mL into the K-D containing the Base/Neutral extract. Rinse the concentrator used for the acid extract with three portions of methylene chloride of for a total of about 25 mL into the K-D containing Base/Neutral extract. Repeat step 8.1.9 to concentrate the combined extract to 5 mL.

8.1.10. Disconnect the concentrator tube from the evaporation flask. Concentrate by flowing nitrogen gas over the concentrator tube to exactly 1 mL. Put the contents into a 2 mL vial. Do not rinse the concentrator tube into the vial with methylene chloride.

8.1.11. Store in refrigerator at 4 °C. Analyze within 40 days.

8.1.12. Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000 mL graduated cylinder. Record the sample volume to the nearest 5 mL.

8.2. Continuous Extraction

8.2.1. Assemble vapor recovery system.

8.2.2. Using a 250 mL graduated cylinder, measure 120 mL methylene chloride. (All glassware must be washed with de-ionized water and soap). Next all of the glassware in use should be solvent rinsed once before use and once after use. Collect the solvents in marked solvent waste bottles. Transfer the solvent to the 250 mL round bottom flask and add 3-4 boiling chips.

8.2.3. Connect the flask to an empty extractor. (Do not forget to use Teflon sleeve on the neck for secure connection). Using a 250 mL graduated cylinder, measure 120 mL methylene chloride. Transfer the solvent to the extractor.

8.2.4. Using a 1 Liter graduated cylinder, measure 1 liter of sample. Slowly transfer the sample to the extractor using a long neck funnel. Add required spike standards (surrogates, lab control standards, matrix spike and matrix spike duplicate). Adjust the PH of the sample to acidic pH (PH<2) and extract acid extractables.

8.2.5. QC includes at least one method blank, 1 LCS (Laboratory Control Standard or Blank Spike), 1 Matrix spike and 1 Matrix spike duplicate per batch. (LCS, MS, MSD should cover at most 20 samples).

8.2.6. All samples should be spiked with Surrogate spiking standard at final concentration of 100 ppm. (50 ul of 2000 ppm BNA Surrogate Spiking Standard.)

8.2.7. Industrial waste liquid samples should be spiked at 100 ppm final concentration (50 µl of 2000 ppm BNA Spiking Standard).

8.2.8. Connect vapor recovery system and turn on cooling water.

8.2.9. Timer set up: press **CHANNEL SELECTOR** until **OUTLET** is selected. Then press **OUTLET ON/OFF** to set **OUTLET ON**. Finally enter **180000**(18 Hours). Press **START** to start timer. Adjust heating mantel controllers to 8. The samples will be extracted for 18 hours.

8.2.10. After 18 hours of extraction, adjust the PH of the samples to pH of 13 or higher with 10 N KOH or NaOH.

8.2.11. Repeat step 8.2.9 (timer setup) and extract for another 18 hours more.

8.2.12. After 36 hours of extraction, the sample is ready for concentration. First pass each extract through a funnel filled with glass wool /Na_2SO_4 and collect the dried extract in Zymark 500-mL flask with 1-mL stem. Rinse the round bottom flask and funnel with Methylene Chloride, collect the rinse solvent in the Zymark 500-mL flask.

Turn on Zymark TurboVap 500 workstation and VWR circulating cooling system.

8.2.13. Set up the Zymark TurboVap 500 workstation water bath temperature at 48 ^{o}C and VWR cooling bath at –2 ^{o}C.

8.2.14. Put the Zymark flask with extracted sample into its place on the TurboVap.

8.2.15. Choose sensor end point on the TurboVap workstation for both samples. Set fan speed at B.

8.2.16. Press start on the TurboVap 500 for both samples.

8.2.17. The TurboVap 500 will stop automatically once it has reached to final volume of 1 mL.

8.2.18. Transfer the samples carefully into pre marked 1 mL vial with 1 mL syringe. If the volume is less than 1 mL, add methylene chloride to 1 mL.

8.2.19. Rinse the Zymark 500-mL flask with Methylene Chloride.

8.2.20. Repeat steps 6.12 thru 6.20 again.

8.3. ACCELERATED SOLVENT EXTRACTION PROCEDURE (ASE, SOLID)

8.3.1. Apparatus and Materials:

8.3.1.1.1. Dionex ASE 200 Accelerated Solvent Extractor equipped with 33-mL stainless steel cells.

8.3.1.1.2. Analytical balance – capable of weighing to 0.01 g.

8.3.1.1.3. Vial for collection of extracts – 60–mL, pre-cleaned, open top screw cap with PTFE-lined silicone septum.

8.3.1.1.4. Filter disk – Type D28.

8.3.1.1.5. Cell cap-sealing disk.

8.3.1.1.6. Oven – drying.

8.3.2. Reagents:

8.3.2.1.1. Dichloromethane, Acetone, Hexane (all pesticide-quality).

8.3.2.1.2. Sodium sulfate (granular anhydrous) – purified by heating at 400 ^{o}C for 4 hours in a shallow tray.

8.3.2.1.3. High purity nitrogen gas – used to purge and/or pressurize the extraction cell.

8.3.2.1.4. Extraction solvent – Acetone/Dichloromethane (1:1, v/v).

8.3.3. Procedure

8.3.3.1. Extraction cell checkup: unscrew the caps from the cell body, check the inside seals and outside O-rings of extraction cell caps, and replace them if necessary to prevent solvent leaks. Rinse extraction cell bodies and caps with Dichloromethane 3 times.

8.3.3.2. Screw one end cap on a cell, and insert a filter disk in the bottom of the cell. Label all cells and corresponding collection vials (each cell should have one collection vial).

8.3.3.3. Turn on nitrogen gas, then ASE power. Check extraction solvent level, solvent bottle pressure (10 psi), system air pressure (50 psi), and compression oven pressure (130 psi). Empty waste vial and rinse vials (total 4). Load method 2.

8.3.3.4. Extraction conditions: (method 2 with automatic rinse between samples)

Extraction solvent:	Acetone/Dichloromethane (1:1, v/v)
Oven temperature:	100 ^{o}C
Pressure:	1500 psi
Heating time:	5 minutes
Static time:	5 minutes
Flush volume:	60% of the cell volume (33-mL cell)
Nitrogen purge:	60 second at 150 psi
Static cycles:	3
Total extraction time:	30 minutes.

Determine water content in sample.

8.3.3.5. Mix 3 grams of sample with an equal amount of anhydrous sodium sulfate (1:1) thoroughly in small baker, until a free-flowing powder is obtained. Use 1:1 for dry sample (sample: sodium sulfate), 1:2 for wet sample, 1:10 ratio if water content is greater than 50%.

8.3.3.6. Transfer the mixture to the extraction cell. Keep threads clean on the cell body and cap.

8.3.3.7. Add surrogate spikes and matrix spikes to the appropriate sample cells.

8.3.3.8. Fill any void volume in the cells with anhydrous sodium sulfate, put second filter disk on top of the anhydrous sodium sulfate, and screw the top cap onto cell body and hand tighten.

8.3.3.9. Begin loading filled cells into the cell tray slots in numerical order. For each sample cell loaded, load a collection vial into the corresponding vial tray position. Press **START** button. The ASE 200 begins running at cell 1 and continues until completing the entire tray (if it is full) or until reaching an empty slot in method mode.

8.3.3.10. Cell 1 should always be an anhydrous sodium sulfate filled blank cell (ASE system blank). There should also be an ASE system blank cell and vial after each known dirty sample cell and vial to prevent contamination.

8.3.3.11. Collect each extract in a clean vial. Allow the extracts to cool after the extractions are complete.

8.3.3.12. Excess water may be present in extracts (very wet sample), and can be removed by filtering the extract through a bed of anhydrous sodium sulfate.

8.3.3.13. For BNA analysis, do base/neutral and acid extractions.

9. CALIBRATION AND SAMPLE ANALYSIS

9.1. Calibration

9.1.1. Before the calibration, the GC/MS must be tuned using perfluorotributylamine (PFTBA). The instrument is tuned according to the manufacturer's recommended values. After the tuning is satisfactory, a solution of ecafluorotripHenylphosphine (DFTPP) is

injected. The ion abundance must meet the criteria listed in Table 4.

9.1.2. Tailing Factor

9.1.2.1. Include with the DFTPP standard is 50 ng of Benzidine and 50 ng of pentachlorophenol. The tailing factor for benzidine must be calculated as a column maintenance test for the base/neutrals. The benzidine-tailing factor must be less than 3.0.

9.1.2.2. The tailing factor for pentachlorophenol must be calculated as a column maintenance test for the acids. The pentachlorophenol-tailing factor must be less than 5.0. The calculation of tailing factor is illustrated in HP ChemStation software.

9.1.3. DDT breakdown (Injector port inertness test)

9.1.3.1. DDT breakdown must be less than 20%

9.1.3.2. 4,4'-DDE and 4,4'-DDD can be located at approximately 1 to 2 minutes before the 4,4'-DDT retention time.

9.1.3.3. For 4,4'-DDE, look for m/z 246. Both DDD and DDT display m/z 235 and 165 in their mass spectra.

9.1.3.4. If degradation of DDT exceeds 20%, maintenance is required on injection port and column.

9.1.3.5. Calculation:

Degradation % = (Sum of TIC areas of DDE and DDD)*100/
(Sum of TIC areas of DDE, DDD and DDT)

9.1.4. Initial Calibration

9.1.4.1. This should be done when the continuing calibration standard fails.

9.1.4.2. After conducting the GC/MS performance tests, establish gas chromatographic operating parameters according section 9.1.5. Internal standard calibration procedure is used to calibrate GCMS.

9.1.4.3. To use this approach, the analyst must select three or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standards is not affected by

method or matrix interferences. Use the base peak m/z as the primary m/z for quantification of the standards. If interferences are noted, use one of the next two most intense m/z quantities for quantification.

9.1.4.4. Prepare calibration standards at five concentration levels in the range of 1 ng/ul to 100 ng/ul for each parameter of interest by adding appropriate volumes of one or more stock standards to a volumetric flask. To each calibration standard or standard mixture, add a known constant amount of one or more internal standards, and dilute to volume with methylene chloride.

9.1.4.5. A minimum of five-point calibration standard is required in the method. The lowest calibration standard should be at a concentration near, but above, the MDL and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC/MS system. Using injections of 1 µL, analyze each calibration standard and tabulate the area of the primary characteristic m/z against concentration for each compound and internal standard. Calculate response factors (RF) for each compound using Equation 1.

Equation 1

$$RF = \frac{(A_S) * (C_{IS})}{(A_{IS}) * (C_S)}$$

Where:

A_S = Area of the characteristic m/z for the parameter to be measured.

A_{IS} = Area of the characteristic m/z for the internal standard.

C_{IS} = Concentration of the internal standard.

C_S = Concentration of the parameter to be measured.

9.1.4.6. The %RSD of the Calibration Check Compounds (CCC) in the initial calibration standard must not exceed 30% and RSD of the rest of the analytes should be less than 15%.

9.1.4.7. The minimum response factor (RF) System Performance Check Compounds (SPCC) must be 0.05.

9.1.4.8. All analytes must be included in the calibration curve. Data from analytes not included in the calibration should not be reported.

9.1.4.9. If the %RSD of any compound is greater than 15%, construct calibration curve of area vs. concentration using 5 points. The correlation coefficient (R square) must be equal to or greater than 0.99.

9.1.5. Continuing calibration verification Standard (CCV)

9.1.5.1. A CCV standard should be analyzed every 12 hours before sample analysis daily after the GCMS has met the tuning criteria.

9.1.5.2. The concentration of the CCV standard should be near the midpoint.

9.1.5.3. All the SPCC compounds must meet a minimum RF of 0.05 and the percent difference (%D) for each CCC compound must be less than 15%.

9.1.6. GC/MS operating conditions

9.1.6.1.1. Instrument Name: BNA #1 (HP 5890 GC/5972 MSD)
Electron energy: 70 eV
Mass range: 35-500 amu
Scan time: 1 sec/scan
Initial column temperature and hold time: 40 °C for 4 min
Column temperature program: 40-270 °C at 10 °C /min
Final column temperature hold: 270 °C (until benzo[ghi]perlene has eluted)
Injector: Grob-type, splitless, 270 °C
Sample volume: 1 μL

Carrier gas: Helium at 1 mL/minute

MS Transfer Line Temperature: 280 °C
MS Source Temperature: 280 °C

9.1.6.1.2. Instrument Name: BNA #2 (HP 5890 GC/5972 MSD)
Electron energy: 70 eV
Mass range: 35-500 amu
Scan time: 1 sec/scan
Initial column temperature and hold time: 40 °C for 4 min
Column temperature program: 40-270 °C at 10 °C /min
Final column temperature hold: 270 °C (until benzo[ghi]perlene has been eluted)
Injector: cool-on-column injection, 230 °C

Sample volume: 1 μL

Carrier gas: Helium at 1 mL/minute

MS Transfer Line Temperature: 280 °C
MS Source Temperature: 280 °C

9.1.6.1.3. Instrument Name: BNA #3 (HP 6890 GC/5973 MSD)
Electron energy: 70 eV
Mass range: 35-500 amu
Scan time: 1 sec/scan
Initial column temperature and hold time: 50 °C for 0.5 min
Column temperature program: 50-100 °C at 10 °C /min
Column temperature program: 100-280 °C at 25 °C /min
Column temperature program: 280-300 °C at 5 °C /min
Final column temperature hold: 300 °C (until benzo[ghi]perlene has eluted)

Injector: Grob-type, splitless, 270 °C

Sample volume: 1 μL
Carrier gas: Helium, Pressure Pulse Program
MS Transfer Line Temperature: 300 °C
MS Source Temperature: 230 °C

9.2. Sample Analysis

9.2.1. Analyst should keep track of the instrument operating condition.

9.2.2. Calibrate MS with FC43 if necessary.

9.2.3. Document all instrument/software problems and maintenance in the instrument logbook.

9.2.4. Inject 1 ul of 50 ng DFTPP solution (including Benzidine, Pentachlorophenol and 4, 4'-DDT).

9.2.5. If DFTPP passes, inject 1 ul of mid-point BNA standard.

9.2.6. If the standard meet the QC criteria stated in this SOP, prepare the extracts for analysis.

9.2.7. The internal standard must be added to sample extract and mixed thoroughly immediately before it is injected into the instrument. This procedure minimizes losses due to adsorption, chemical reaction or evaporation.

9.2.8. Inject 1 µL of the sample extract or standard into the GC/MS system.

9.2.9. If the response for any m/z exceeds the working range of the GC/MS system, dilute the extract and reanalyze.

9.2.10. Perform all qualitative and quantitative measurements as described in Sections 10. When the extracts are not being used for analyses, store them refrigerated at 4°C, protected from light in screw-cap vials equipped with unpierced Teflon-lined septa.

10. CALCULATION

10.1. Qualitative Identification

10.1.1. Obtain EICPs for the primary m/z and the two other masses listed in Tables 4 and 5 of EPA Method 625. The following criteria must be met to make a qualitative identification:

10.1.1.1.1. The characteristic masses of each parameter of interest must maximize in the same or within one scan of each other.

10.1.1.1.2. The retention time must fall within 30 seconds of the retention time of the authentic compound.

10.1.1.1.3. The relative peak heights of the three characteristic masses in the EICPs must fall within 20% of the relative intensities of these masses in a reference mass spectrum. The reference mass spectrum can be obtained from a standard analyzed in the GC/MS system or from a reference library.

10.1.2. Structural isomers that have very similar mass spectra and less than 30 seconds difference in retention time, can be explicitly identified only if the resolution between authentic isomers in a standard mix is acceptable. Acceptable resolution is achieved if the baseline to valley height between the isomers is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

10.2. Calculations

10.2.1. When a parameter has been identified, the quantitation of that parameter will be based on the integrated abundance from the EICP of the primary characteristic m/z in Tables 4 and 5 of EPA Method

625. Use the base peak m/z for internal and surrogate standards. If the sample produces an interference for the primary m/z, use a secondary characteristic m/z to quantitate.

Calculate the concentration in the sample using the response factor (RF) determined in Section 7.2.2 and Equation 2.

Equation 2

$$\text{Concentration (ug/L)} = \frac{(A_s) * (I_s)}{(A_{IS}) * (RF) * (V_0)}$$

Where:

A_S = Response for the parameter to be measured.
A_{IS} = Response for the internal standard.
I_S = Amount of internal standard added to each extract (µg).
V_O = Volume of water extracted (L).

10.2.2. Report results in µg/L without correction for recovery data. All QC data obtained should be reported with the sample results.

11. QUALITY ASSURANCE AND QUALITY CONTROL

11.1. The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is shown when the analyst meets all QC Acceptance Criteria.

11.2. DFTPP shall be analyzed to confirm that all the key m/z criteria in Table 4 are achieved prior to analysis of samples.

11.3. The initial and CCV standards must meet the QC requirements listed in the calibration section in this SOP.

11.4. A method blank and a LCS (Lab Control Sample, de-ionized water spike) will be analyzed for each batch of samples. A Matrix Spike (MS) and a matrix spike duplicate shall be analyzed at the rate of one per 20 samples or fewer.

11.5. The method blank should not have any target analytes at or above the method reporting limit and all surrogates in the method blank should be within the control limit.

11.6. The surrogates in a sample should fall in control range chart (section 11.8). One acid and one base/neutral surrogate in a sample can fall outside the control limit.

11.7. The spike recoveries of all the analytes in LCS and MS/MSD must meet QC limits, which are derived from historical data.

11.8. Quality control chart - Quality control chart is a graphical representation of various deviations of data within an interval length of time.

11.8.1. As part of the QC program for the laboratory, method accuracy and precision must be assessed and records must be maintained. On an on–going basis, after the analysis of samples, LCS and spiked wastewater samples, calculate the percent recovery (p), average percent recovery (P) and the standard deviation of the percent recovery (s) for surrogates and spiked analytes . Express the accuracy assessment as a percent interval from -2s to +2s (lower and upper control limit). If P = 90% and s =10%, for example, the accuracy interval is expressed as 70-110%.

11.8.2. Make a quality control chart by plotting RECOVERY (%) vs. NUMBER of spiked wastewater samples or LCS for each analyte, and RECOVERY (%) vs. NUMBER of samples for each surrogate based on accuracy assessment. Update the quality control chart for each parameter on a regular basis: every four months. In the QC chart, it should have average recovery (P), lower control limit (P – 2s) and upper control limit (P+ 2s), and actual recovery (p) for each analyte.

11.8.3. This QC chart kept in this manner serves as a floating control range chart. This floating control range must be within limits specified by EPA Methodology.

Table 1—Base/Neutral Extractables

Parameter	STORET No.	CAS No.
Acenaphthene	34205	83-32-9
Acenaphthylene	34200	208-96-8
Anthracene	34220	120-12-7
Benzo(a)anthracene	34526	56-55-3
Benzo(b)fluoranthene	34230	205-99-2
Benzo(k)fluoranthene	34242	207-08-9
Benzo(a)pyrene	34247	50-32-8
Benzo(ghi)perylene	34521	191-24-2
Benzyl butyl phthalate	34292	85-68-7
Bis(2-chloroethyl)ether	34273	111-44-4
Bis(2-chloroethoxy)methane	34278	111-91-1
Bis(2-ethylhexyl)phthalate	39100	117-81-7
Bis(2-chloroisopropyl)ether	34283	108-60-1
4-Bromophenyl phenyl ether	34636	101-55-3
2-Chloronaphthalele	34581	91-58-7
4-Chlorophenyl phenyl ether	34641	7005-72-3
Chrysene	34320	218-01-9
Dibenzo(a,h)anthracene	34556	53-70-3
Di-n-butylphthalate	39110	84-74-2
1,3-Dichlorobenzene	34566	541-73-1
1,2-Dichlorobenzene	34536	95-50-1
1,4-Dichlorobenzene	34571	106-46-7
3,3'-Dichlorobenzidine	34631	91-94-1
Diethyl phthalate	34336	84-66-2
Dimethyl phthalate	34341	131-11-3
2,4-Dinitrotoluene	34611	121-14-2
2,6-Dinitrotoluene	34626	606-20-2
Di-n-octylphthalate	34596	117-84-0
Fluoranthene	34376	206-44-0
Fluorene	34381	86-73-7
Hexachlorobenzene	39700	118-74-1
Hexachlorobutadiene	34391	87-68-3
Hexachloroethane	34396	67-72-1
Indeno(1,2,3-cd)pyrene	34403	193-39-5
Isophorone	34408	78-59-1
Naphthalene	34696	91-20-3
Nitrobenzene	34447	98-95-3
N-Nitrosodi-n-propylamine	34428	621-64-7
Phenanthrene	34461	85-01-8
Pyrene	34469	129-00-0
1,2,4-Trichlorobenzene	34551	120-82-1

Table 2--Acid Extractables

Parameter	STORET No.	CAS No.
4-Chloro-3-methylphenol	34452	59-50-7
2-Chlorophenol	34586	95-57-8
2,4-Dichlorophenol	34601	120-83-2
2,4-Dimethylphenol	34606	105-67-9
2,4-Dinitrophenol	34616	51-28-5
2-Methyl-4,6-dinitrophenol	34657	534-52-1
2-Nitrophenol	34591	88-75-5
4-Nitrophenol	34646	100-02-7
Pentachlorophenol	39032	87-86-5
Phenol	34694	108-95-2
2,4,6-Trichlorophenol	34621	88-06-2
2-methylphenol *	not required	
4-methylphenol *	not required	
2,4,5-Trichlorophenol *	not required	

Table 3—Additional Extractable Parameters a

Parameter	STORET No.	CAS No.
Benzidine	39120	92-87-5 605
Hexachlorocylopentadiene	34386	77-47-4 612
N-Nitrosodimethylamine	34438	62-75-9 607
N-Nitrosodiphenylamine	34433	86-30-6 607
1,2-Diphenylhydrazine	not required but on NPDES permit	

TABLE 4	
DFTPP KEY IONS AND ION ABUNDANCE CRITERIA	
MASS	ION ABUNDANCE CRITERIA
51	30-60% OF MASS 198
68	<2% OF MASS 69
70	<2% OF MASS 69
127	40-60% OF MASS 198
197	<1% OF MASS 198
198	BASE PEAK, 100% RELATIVE ABUNDANCE
199	5-9% OF MASS 198
275	10-30% OF MASS 198
365	>1% OF MASS 198
441	PRESENT BUT LESS THAN MASS 443
442	>40% OF MASS 198
443	17-23% OF MASS 442

City of Los Angeles

ENVIRONMENTAL MONITORING DIVISION

Instrumental Chemistry Strategic Business Unit
Semi – Volatile Organic Laboratory

STANDARD OPERATING PROCEDURE for

Chlorinated Pesticides by Gas Chromatography

(EPA Method 8081A) SOP# XXXX

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1. Scope and Application

1.1. This is a solid waste method in accordance with the requirements set in the EPA NPDES permit for the operation of the Hyperion Treatment Plant, and Terminal Island Treatment Plants, it is necessary to analyze for the following Pesticides:

	COMPONENTS	STANDARD USED
1)	ALDRIN	MIX AB
2)	A-BHC	MIX AB
3)	B-BHC	MIX AB
4)	D-BHC	MIX AB
5)	G-BHC	MIX AB
6)	CHLORDANE	INDIVIDUAL
7)	CHLORDANE (5-COMPONENTS)	INDIVIDUAL
8)	DIELDRIN	MIX AB
9)	ENDRIN	MIX AB
10)	ENDOSULFAN I	MIX AB
11)	ENDOSULFAN II	MIX AB
12)	ENDOSULFAN II SULFATE	MIX AB
13)	ENDRIN ALDEHYDE	MIX AB
14)	HEPTACHLOR	MIX AB
15)	HEPTACHLOR EPOXIDE	MIX AB
16)	METHOXYCHLOR	MIX AB
17)	MIREX	MIX AB
18)	O, P'-DDE	MIX AB
19)	O, P'-DDD	MIX AB
20)	O, P'-DDT	MIX AB
21)	P, P'-DDE	MIX AB
22)	P, P'-DDD	MIX AB
23)	P, P'-DDT	MIX AB
24)	TOXAPHENE	INDIVIDUAL

1.2. This is a Gas Chromatographic (GC), Electron Capture Detector Method applicable to the determination of organochlorine pesticide, which are man-made, extremely hazardous and are very persistent in the environment. Most of the pesticides determined by this procedure are currently illegal to use but they are still frequently detected in samples because of their persistence.

1.3. This method is applicable to either liquid (ground water, landfill condensate) or solids (soil, sediment, tissue).

2. Summary of Method

2.1. A measured volume or weight of sample (approximately 1 L for liquids, 3 g for solids) is extracted using the appropriate matrix-specific sample extraction technique.

2.2. Liquid samples are extracted with methylene chloride using continuous liquid-liquid extraction (CE). The CE extract is solvent exchanged to hexane and concentrated for florisil cleanup and sulfur cleanup.

2.3. Solid samples are extracted with methylene chloride-acetone (1:1) using accelerated solvent extraction (ASE). The ASE extract is solvent exchanged to hexane and concentrated for Acetonitrile cleanup, florisil cleanup and sulfur cleanup.

2.4. A Gas Chromatograph with its parameters established to permit the separation and measurement of the pesticides by Electron Capture Detector (ECD) is used to identify and quantify the target compounds in samples.

2.5. Compound identification based on primary-column analysis should be confirmed on a second column.

3. Interferences: Sources of interference in this method can be grouped into three broad categories.

3.4 Contaminated solvents, reagents, or sample processing hardware.

3.5 Contaminated GC carrier gas, parts, column surfaces, or detector surfaces.

3.6 Compounds extracted from the sample matrix to which the detector will respond.

3.4 Interferences co-extracted from the samples will vary considerably from waste to waste.

4. Sample Collection, preservation, and Holding Time

4.2. Before use, all sample containers are washed with soap and tap water, rinsed with hexane, and dried. Care must be taken to avoid contact with plastic to minimize Phthalate interference's in the analyses.

4.3 Liquid samples are collected in 1000 ml or 1/2 gallon glass bottles with Teflon lined caps. Liquid samples are stored at 4 ^{o}C and must be extracted within 7 days. The extracts must be analyzed within 40 days.

4.4 Solid samples (sludge, tissue, and sediment) are collected in appropriately

Sized (2-4 oz) glass containers with Teflon lined caps. Solid samples are stored at 4 ^{o}C or frozen. Solid samples are extracted within 14 days and if frozen (e.g., tissue & sediment) must be extracted within 6 months.

5. Chain of Custody and Sample Registry

5.1. All samples received by the Sample Receiving Unit. The samples are logged into LIMS and stored at 4 ^{o}C. The Organic Unit receives samples from the sample receiving unit for analysis.

5.2. Samples will be logged into organic logbook and a copy of chain of custody will be kept in work order book.

6. Apparatus

6.1. Glassware

- Continuous extraction glassware
- 125 ml separatory funnel with teflon stopcock and glass stopper
- 1 L beaker
- 250 ml beaker
- 100 mm long-stemmed funnel
- Kuderna-Danish (K/D) flask, 250 ml
- 250 ml round bottom flask
- graduated ampoule
- ungraduated ampoule
- Snyder column (three ball)
- 500 ml graduated cylinder
- chromatographic column with reservoir
- 5 ml vials with teflon septa
- 60 ml vials with teflon septa
- dispensing flask

6.2 Equipment and Materials

- ASE 200 accelerated solvent extractor and accessory
- Double beam balance
- Centrifuge
- Waterbath
- Solvent evaporation unit
- Nitrogen stream evaporation unit
- Glass wool
- Boiling chips (soxhlet extracted or put in furnace at 400^{0}C)

- Clamps (various sizes)
- Tweezers
- Thimbles
- Heating mantles and controls
- Timers

6.3 Gas Chromatograph

The following GC/ECD systems are available for analysis:

a) **Gas Chromatograph- HP 5890**
Data station with Window NT and HP ChemStation Enviroquant software
Dual Electron Capture Detectors
Autosampler (HP 7673)
Columns:
Primary: DB5-60 m length, 0.32 mm diameter.
Confirmation: DB-XLB 60 m length, 0.32 mm diameter.

On Column Dual Injection (two independent injectors)
HP LaserJet 4 printer

HP5890 Temperature Program for All Samples:

Detector Temperature: 300 ^{O}C

Injector Temperature: 250 ^{O}C

Oven Program:

Initial Temperature 120 ^{O}C
Initial Time 0.5 Minutes

Level	Rate (C/min)	Final Temp (^{O}C)	Final Time (min)
1	5.0	160	0.00
2	3.0	260	3.0

Total Program Time: 44.83 Minutes

Inlet A Pressure Values:

Constant Flow: On
Pressure: 267 kpa
Temperature 120 ^{O}C

Inlet B Pressure Values:

Constant Flow: On
Pressure: 111 kpa
Temperature: 120 ^{O}C

b) **Gas Chromatograph- HP 6890**

Data station-Kayak with Windows NT and HP ChemStation Enviroquant software

Electron Capture Detector
Autosampler (HP 6890 series)
Columns:

Primary: HP-5 30m length, 0.320-mm id.
Confirmation: DB-1701 30m length, 0.320-mm id.

Dual Injectors – fast inject
HP LaserJet 4000 printer

HP6890 Temperature Program for All Samples:

Detector Temperature: 300 ^{O}C
Oven Program:

Initial Temperature 100 ^{O}C
Initial Time 2.0 Minutes

Level	Rate (^{O}C /min)	Final Temp (^{O}C)	Final Time (min)
1	15.0	160	0.00
2	4.0	265	5.00

Total Program Time: 37.25 Min

Inlet Temperature/Pressure Information for Both Inlet A and B:

Initial Temperature 250 ^{O}C (On)
Initial Time 2.0 Minutes
Mode: Pulsed Splitless
Pressure: 63.4 kpa (On)-Injector A
Pressure: 56.4 kpa (On)-Injector B
Pulse Pressure: 172 kpa
Pulse Time: 0.75 min.
Purge Flow: 0.75 mL/min
Total Flow: 64.0 mL/min(A);63.9 mL/min(B)

Gas Saver: On
Saver Flow: 20 mL/min
Saver Time: 3.00 min
Gas Type: Helium

Pressure Program:

GC Pressure Units: kpa
Entered Values:
Column Length: 30m
Column Diameter: 0.320 mm
Gas: Helium
Vacuum Comp: Off

Column 1	Column 2
Hp-5 5% Methyl Siloxane	DB-1701
Mode: Constant Flow	Mode: Ramped Flow
Initial flow: 1.5 mL/min	Initial flow: 1.3 mL/min
Nominal Initial Pressure: 63.4 kpa	Nom. Initial Pressure: 56.4 kpa
Average Velocity: 29 cm/sec	Average Velocity: 26 cm/sec

Ramped Flow Program for Column 2

#	Rate	Final Flow	Final Time
1	40.00	5.0	5.00
2	40.00	1.0	28.00
5	0.0 (Off)		

Post Flow: 0.0 mL/min

c) **Gas Chromatograph- Varian 3800 GC-ECD**
See attached GC method for operating parameter.

7. Chemicals & Reagents

7.1. Chemicals

- Hexane - pesticide grade
- Methylene Chloride - pesticide grade
- Acetone
- Acetonitrile
- Ethyl ether - pesticide grade
- Florisil (60/100 mesh)

- Sodium sulfate (granular)
- Copper (granular)

7.2. Standards

7.2.1 All standards should be at least 96% pure and are generally purchased ChemService (primary standards). Second source standards are purchased from Ultra Scientific. All standards are prepared in hexane in volumetric flasks and stored in amber bottles with Teflon lined caps at 4 ^{0}C.

7.2.2 Five calibration concentrations are prepared for each standard or set of standards. New standards are prepared within 6 months (or sooner if signs of degradation are apparent). Newly prepared standards are compared with second source standards. If they are not within 20%, the standards are verified against a third source.

8. Extraction

8.3. All samples undergoing extraction are entered into the extraction logbook. This book contains the sample log number, date extraction started, date extraction finished, spike amount, date of florisil, sulfur clean up, final volume, date concentrated, and initials of person conducting extraction.

8.2. Liquid samples are extracted with methylene chloride using continuous liquid-liquid extraction (CE). The CE extract is solvent exchanged to hexane and concentrated for florisil cleanup and sulfur cleanup. Refer **Appendix-**A for Continuous Extraction and **Appendix-B** for cleanup procedures.

8.4. Solid samples are extracted with methylene chloride-acetone (1:1) using accelerated solvent extraction (ASE). The ASE extract is solvent exchanged to hexane and concentrated for Acetonitrile cleanup, florisil cleanup and sulfur cleanup. Refer **Appendix-C** for Accelerated Solvent Extraction, **Appendix-D** for Acetonitrile cleanup procedures and **Appendix-B** for florisil and sulfur cleanup procedures.

9. Gas Chromatograph

9.1 Documentation

From organic logbook, samples are logged to the pesticides extraction book, with different categories such as: plant, sediment, tissue, special, biosolids.

9.2 Instrument set up

see 6.3

9.3. Calibration

9.3.1 Initial Calibration

The external standard calibration procedure is used for this method. Five concentration levels of each analyte are prepared for calibration purpose. The lowest calibration standard is at a concentration equivalent to the minimum reporting level.

The calibration factor (*CF*) for each analyte at each concentration, the mean calibration factor (*CF*), and the relative standard deviation (*RSD*) of the calibration factors are calculated by using the formulae below.

$$CF = \frac{A}{C}$$

A - Peak area of the compound in the standard
C – Concentration of the compound

$$\text{Mean CF} = \overline{CF} = \sqrt{\frac{\sum_{i=1}^{n} \{CF_i - \overline{CF}\}^2}{n-1}}$$

$$RSD = \frac{SD}{\overline{CF}} * 100$$

The acceptance criteria for the initial calibration is that the relative standard deviation (RSD) of the calibration factors is less than 20%. The mean calibration factor can be used to quantitate sample results.

Alternatively, if the RSD is greater than 20%, a calibration curve can be used for quantitation with r-squared value greater than 0.99.

For multi-component analytes, 7 - 10 characteristic peaks are used in the initial calibration.

9.3.2. Daily Calibration

Once the initial calibration established, the working calibration must be verified every 12 hours by injecting a mid point standard (continuing calibration standard).

The acceptance criteria for the daily calibration is that the RPD (relative percent difference), must be less or equal to +/- 15% before any sample is analyzed.

$$RPD = |CF - \overline{CF}| * 100 / (\overline{CF})$$

If any analyte fails this criteria, but the average of the responses for all analytes meets this criteria, the calibration is verified. If the verification does not meet the criteria, a new five point calibration should be prepared and run.

9.3.3 At the beginning of each run, and once every 12 hours while the run is in progress, the instrument must be shown to be capable of delivering acceptable data by making sure that the following performance criteria are met:

9.3.3.1 The column must be free from front-end damage.
9.3.3.2. The injector and injector liner must be clean.
9.3.3.3 The column must be in good enough condition to meet proven linearity of response standards.
9.3.3.4 The RPD (relative percent difference) must be less or equal +/- 15%.

9.3.4 GC operation (sample analysis)

9.3.4.1 The same GC operating conditions used for the initial calibration must be employed for samples analyses.

9.3.4.2 Verify calibration by analyzing mid-point standard every 12 hours and meeting the criteria in 9.3.2 and 9.3.3 prior to conducting sample analysis. A calibration standard should be injected at interval of every 20 samples.

9.3.4.3 The Endrin and DDT degradation standard should be analyzed at the beginning of each working day, subsequently after each 20 runs, and at the end of analytical sequence. The degradation must be less than 15% for both Endrin and DDT. Otherwise instrument maintenance is required.

9.3.4.4 One method blank is analyzed with each set of 20 or fewer samples. The blank results must be less than the MDL. No blank values will be subtracted from the sample values.

9.3.4.5 Inject a 1-µL aliquot of the concentrated sample extract (fraction A and B). Record the volume injected and the resulting peak size in area units.

9.3.4.6 Qualitative identifications of target analytes are made by examination of the sample chromatograms, as described in Section 10.

9.3.4.5 Quantitative results are determined for each identified compound, using the procedures described in section 11 for the

external calibration procedure. If the responses in the sample chromatogram exceed the calibration range of the system, dilute the extract and reanalyze.

9.3.4.6 In an autosampler run, hexane is run after at least every 20 samples to check for carryover.

10. Identification

10.1 single component analytes are identified by comparing their retention time in sample to that of standard. A retention time difference of plus or minus 0.05 minute from standard confirms presence of the compound in sample. All compounds identified in primary column must be confirmed on a second column with different packing materials.

10.2 For multi-component compounds, the following criteria must be met:

10.2.1 At least 5 of the characteristic peaks must be within plus or minus 0.05 minute of the retention time of their corresponding peak in the standard.

10.2.2 Pattern recognition - the ratio of the peaks in the sample to those in the standard should be consistent within the limitations imposed by the matrix.

10.2.3

11. Quantitation

11.1 Quantitation of target compounds: average response factor (RF) or calibration factor (CF) from initial calibration is used for quantitation of target compounds.

11.2 Quantitation of Toxaphene and Chlordane

After running and reprocessing the chromatogram of the sample to be analyzed, the concentration of 5-7 peaks of the 7 - 10 characteristic peaks chosen in the initial calibration that are closest in value for the sample are added together and the mean is calculated. This mean value is reported as the analytical result of the analysis for the given multipeak component.

The reason for choosing the 5-7 closest of the 7 - 10 results is that in samples that are extremely dirty and/or those that have complex matrices, there invariably occurs some co-elution of other components or of unidentified peaks in the matrix with at least one or two of the peaks selected for quantitation. The choice of the 5-7 closest peaks removes some of the variation in value caused by co-elution and matrix interference.

12. Data Processing

The data from the GC run must be reprocessed. This reprocessing includes setting the integration events to draw baselines properly on the chromatogram. In some cases manual integration will be necessary to insure that everything is integrated correctly. Make sure that the data station will calculate the results using average response factors of the 5-point calibration curve.

13. QC Procedure

13.1 All extraction and spike information is recorded in the extraction logbook

.

13.2 A method blank(MB) is analyzed with every batch of samples (20 or less samples per batch). The MB must be less than Method Reporting Limit(MRL). No blank values will be subtracted from the sample values.

13.3 A distilled water spike or clean sand spike (LCS, QC check) is analyzed with every batch of samples (20 or less samples per batch). LCS recoveries must be within laboratory established acceptance limits for all target analytes.

13.4 One matrix spike (MS and one matrix spike duplicate (MSD) pair is analyzed with each set of 20 or fewer samples. MS/MSD recoveries must be within laboratory established acceptance limits for all target analytes.

13.5 The Endrin/PT degradation standard is analyzed at the beginning of each working day, subsequently after each 20 runs, and at the end of the analytical sequence. Compound degradation must be less than 15 % for both compounds. If the degradation is greater than 15%, the instrument can not be used for sample analysis and maintenance is required. Analysis can not resume until the degradation standard passes the above criteria.

13.6 The percent relative standard deviation (%RSD) of the response factors (CF) of 5 point calibration should be less than 20%. If the %RSD is greater than 20%, the r-squared value must be greater than 0.99 to use calibration curve for Quantitation.

13.7 The RPD (relative percent difference) for daily calibration must be less or equal +/- 15%.

13.8 Results may be reported from either column of dual column system, provided that all QC criteria are met on the column used for reporting purpose.

13.9 Any sample that has a positive result greater than the value of the highest standard must be diluted and re-analyzed.

13.10 Positive results should be confirmed on the secondary column within 50% RPD of primary column results. Since it is possible for analytes to be present and be outside

the confirmation acceptance criteria, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

13.11 QC charts for all matrixes and LSC are updated after each 5- 10 batches of analysis. Corrective actions are taken if any deviation in analysis is observed. This QC chart serves as a floating control range chart.

13.12 Solutions from which spiking solutions are made need to be purchased either from a different manufacturer than the one from which Standard solutions are made, or from a different lot# from the same manufacturer. In addition, a 3rd set of solutions should be available, such as ERA or EPA standard solutions. These solutions can be used to check the accuracy of the solutions obtained from other manufacturers.

13.13 Retention time study: Make three injections of standard over the course of 72 hours. Record the retention time and calculated the mean and standard deviation of the three retention times for each analytes and surrogate. The width of the retention window for each analyte and surrogate is defined as +/- 3 times the standard deviation of the mean retention time. Establish the center of the retention time window for each analyte and surrogate by using the retention time from the calibration verification standard at the beginning of the analytical shift.

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STANDARD OPERATING PROCEDURE for

Polychlorinated Biphenyls(PCBs) by Gas Chromatography

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TABLE OF CONTENTS

1. Scope and Application

1.1. This is a solid waste method that is used to determine the concentrations of polychlorinated biphenyls (PCBs) as Aroclors in extracts from solid and aqueous matrices. The target compounds are listed below:

	COMPOUNDS	STANDARD USED
1)	AROCLOR 1016	MIX OF AROCLOR 1016&1260
2)	AROCLOR 1221	INDIVIDUAL
3)	AROCLOR 1232	INDIVIDUAL
4)	AROCLOR 1242	INDIVIDUAL
5)	AROCLOR 1248	INDIVIDUAL
6)	AROCLOR 1254	INDIVIDUAL
7)	AROCLOR 1260	MIX OF AROCLOR 1016&1260

1.2 This is a Gas Chromatographic (GC), Electron Capture Detector Method with dual-column and dual-detector. Compound identification based on the first column analysis will be confirmed on a second column.

1.3 Aroclors are multi-component mixtures. When samples contain more than one Aroclor, a higher level of analyst expertise is required to attain acceptable levels of qualitative and quantitative analysis.

1.4. This method is applicable to either liquid (ground water, landfill condensate) or solids (soil, sediment, tissue).

3. Summary of Method

3.1. A measured volume or weight of sample (approximately 1 L for liquids, 3 g for solids) is extracted using the appropriate matrix-specific sample extraction technique.

3.2. Liquid samples are extracted with methylene chloride using continuous liquid-liquid extraction (CE). The CE extracts are solvent exchanged to hexane and concentrated for florisil cleanup and sulfur cleanup.

3.3. Solid samples are extracted with methylene chloride-acetone (1:1) using accelerated solvent extraction (ASE). The ASE extracts are solvent exchanged to hexane and concentrated for Acetonitrile cleanup, florisil cleanup and sulfur cleanup.

3.4. A Gas Chromatograph with its parameters established to permit the separation and measurement of the PCBs by Electron Capture Detector (ECD) is used to identify and quantify the target compound in samples.

3.5. Compound identification based on the first column analysis should be confirmed on a second column.

4. Interferences:

Sources of interference in this method can be grouped into three broad categories.

3.7 Contaminated solvents, reagents, or sample processing hardware.

3.8 Contaminated GC carrier gas, parts, column surfaces, or detector surfaces.

3.9 Compounds extracted from the sample matrix to which the detector will respond.

3.4 Interferences co-extracted from the samples will vary considerably from waste to waste.

4. Sample Collection, preservation, and Holding Time

4.3. Before use, all sample containers are washed with soap and tap water, rinsed with hexane, and dried. Care must be taken to avoid contact with plastic to minimize Phthalate interference's in the analyses.

4.5 Liquid samples are collected in 1000 ml or 1/2 gallon glass bottles with Teflon lined caps. Liquid samples are stored at 4 ^{o}C and must be extracted within 7 days. The extracts must be analyzed within 40 days.

4.6 Solid samples (sludge, tissue, and sediment) are collected in appropriately sized (2-4 oz) glass containers with Teflon lined caps. Solid samples are stored at 4 ^{o}C or frozen. Solid samples are extracted within 14 days and if frozen (e.g., tissue & sediment) must be extracted within 6 months.

5. Chain of Custody and Sample Registry

6.1. All samples will be received by the Sample Receiving Unit. The samples are then logged into LIMS and stored at 4 ^{o}C. The Organic Unit receives samples from the sample receiving unit for analysis.

6.2. Samples will be logged into organic logbook and a copy of chain of custody will be kept in work order book.

7. Apparatus and Materials

6.1. Glassware

- Continuous extraction glassware
- 125 ml separatory funnel with teflon stopcock and glass stopper
- 1 L beaker
- 250 ml beaker
- 100 mm long-stemmed funnel
- Kuderna-Danish (K/D) flask, 250 ml
- 250 ml round bottom flask
- graduated ampoule
- ungraduated ampoule
- Snyder column (three ball)
- 500 ml graduated cylinder
- chromatographic column with reservoir
- 5 ml vials with teflon septa
- 60 ml vials with teflon septa
- dispensing flask

6.2 Equipment and Materials

- ASE 200 accelerated solvent extractor and accessory
- Double beam balance
- Centrifuge
- Waterbath
- Solvent evaporation unit
- Nitrogen stream evaporation unit
- Glass wool
- Boiling chips (soxhlet extracted or put in furnace at 400^0C)
- Clamps (various sizes)
- Tweezers
- Thimbles
- Heating mantles and controls
- Timers

6.3 Gas Chromatograph

Varian 3800 GC-ECD #2

See attached GC method for operating parameters.

HP 5890 GC-ECD

See attached GC method for operating parameters

HP 6890 GC-ECD

See attached GC method for operating parameters

7. Chemicals & Reagents

7.1. Chemicals

- Hexane - pesticide grade
- Methylene Chloride - pesticide grade
- Acetone
- Acetonitrile
- Ethyl ether - pesticide grade
- Florisil (60/100 mesh)
- Sodium sulfate (granular)
- Copper (granular)

7.2. Standards

7.2.1 All calibration standards should be at least 96% pure and are generally purchased ChemService (primary standards). Second source standards and LCS spike standards are purchased from Ultra Scientific. All standards are prepared in hexane except LCS spiking standards (in methanol), with volumetric flasks and stored in amber bottles with Teflon lined caps at 4 ^{0}C.

7.2.4 Five calibration concentrations are prepared for each standard or set of standards. New standards are prepared within 6 months (or sooner if signs of degradation are apparent). Newly prepared standards are compared with second source standards. If they are not within 20%, the standards are verified against a third source.

7.2.5 See Attachment for standard preparation.

8. Extraction

8.5. All samples undergoing extraction are entered into the extraction logbook. This book contains the sample log number, date extraction started, date extraction finished, spike amount, date of florisil, sulfur clean up, final volume, date concentrated, and initials of person conducting extraction.

8.2. Liquid samples are extracted with methylene chloride using continuous liquid-liquid extraction (CE). The CE extract is solvent exchanged to hexane and concentrated for florisil cleanup and sulfur cleanup. Refer **Appendix-**A for Continuous Extraction and **Appendix-B** for cleanup procedures.

8.6. Solid samples are extracted with methylene chloride-acetone (1:1) using accelerated solvent extraction (ASE). The ASE extract is solvent exchanged to hexane and concentrated for Acetonitrile cleanup, florisil cleanup and sulfur cleanup. Refer **Appendix-C** for Accelerated Solvent Extraction, **Appendix-D** for Acetonitrile cleanup procedures and **Appendix-B** for florisil and sulfur cleanup procedures.

9. Gas Chromatograph

9.1 Documentation

Analyst will write his/her initial and date in extraction logbook before analysis starts. The raw data, originally stored on the hard disk, is transferred to Virtual Drive for long term storage.

9.2 Instrument setup

see 6.3

9.3. Calibration

9.3.1 A standard containing a mixture of Aroclor 1016 and Aroclor 1260 will include many of the peaks represented in the other five Aroclor mixtures. As a result, a multi-point initial calibration employing a mixture of Aroclors 1016 and 1260 at five concentrations should be sufficient to demonstrate the linearity of the detector response without the necessity of performing initial calibrations for each of the seven Aroclors.

9.3.2 The mixture of Aroclors 1016 and 1260 at five concentrations can be used as a standard to demonstrate that a sample does not contain peaks that represent any one of the Aroclors. This standard can also be used to determine the concentrations of either Aroclor 1016 or Aroclor 1260, should they be present in a sample.

9.3.3 Single standards of each of the other five Aroclors are required to aid the analyst in pattern recognition. Assuming that the Aroclor 1016/1260 standards described in Sec. 9.3.1 have been used to demonstrate the linearity of the detector, these single standards of the remaining five Aroclors are also used to determine the calibration factor for each Aroclor.

9.3.4 Initial Calibration

5 to 10 characteristic peaks are chosen for calibration.

Initial calibration is performed for these peaks using 5 concentration levels. The calibration is by the external standard method.

When external standard calibration is employed, calculate the calibration factor (*CF*) for each peak at each concentration, the mean calibration factor (*CF*), and the relative standard deviation (*RSD*) of the calibration factors, using the formulae below.

$$CF = \frac{A}{C}$$

A - Peak area of the compound in the standard
C – Concentration of the compound

$$\text{Mean } CF = \overline{CF} = \sqrt{\frac{\sum_{i=1}^{n} \{CF_i - \overline{CF}\}^2}{n-1}}$$

$$RSD(\%) = \frac{SD}{\overline{CF}} * 100$$

The acceptance criteria for the initial calibration curve is the relative standard deviation (RSD) less than 20%.

9.3.5. Daily Calibration

Once the initial calibration established, a mid point standard (continuing calibration standard) is run and compared against the 5 point calibration curve. Calculate the relative percent difference (RPD) as

$$RPD = |CF - \overline{CF}| * 100 / (\overline{CF})$$

The acceptance criteria for the daily calibration is that

the RPD (relative percent difference), must be <15% for all characteristic peaks selected for the initial calibration before any sample is analyzed. If this criterion is not met, corrective action, possibly including a new 5-point calibration, should be taken.

9.3.6 At the beginning of each run, and once every 12 hours while the run is in progress, a mid point standard (continuing calibration standard) is run and compared against the 5 point calibration curve.

9.3.7 GC operation

9.3.7.1 The same GC operating conditions used for the initial calibration must be employed for samples analyses.

9.3.7.2 Verify calibration by analyzing mid-point standard every 12 hours and meeting the criteria in 9.3.5 prior to conducting sample analysis. A calibration standard should be injected at interval of every 20 samples. For Aroclor analyses, the calibration verification standard should be a mixture of Aroclor 1016 and Aroclor 1260. The calibration verification process does not *require* analysis of the other Aroclor standards used for pattern recognition.

9.3.7.3 Inject a 1-µL aliquot of the concentrated sample extract (fraction A only for PCBs as Aroclors). Record the volume injected and the resulting peak size in area units.

9.3.7.4 Qualitative identifications of target analytes are made by examination of the sample chromatograms, as described in Section 10.

9.3.7.5 Quantitative results are determined for each identified Aroclors, using the procedures described in section 11 for the external calibration procedure. If the responses in the sample chromatogram exceed the calibration range of the system, dilute the extract and reanalyze.

9.3.7.6 In an autosampler run, hexane is run after at least every 10 samples to check for carryover.

10. Identification of PCBs as Aroclors

10.1 The identification of PCBs as Aroclors using this method with an electron capture detector is based on agreement between the retention times of peaks in the sample chromatogram with the retention time windows established through the analysis of standards of the target analytes. Target compounds are identified by comparing their retention time in sample to that of standard.

10.2Tentative identification of any Aroclor occurs when at least 5 of the characteristic peaks (5 to 10 peaks) from a sample extract falls within the established retention time window for that Aroclor. A retention time difference of plus or minus 0.05 minute for all 5 peaks from standard confirms presence of the compound in sample. Each tentative identification must be confirmed by using a second GC

column of dissimilar stationary phase, based on a clearly identifiable Aroclor pattern.

10.3 The pattern in the sample chromatogram should be compared to that of the standard to ensure that all the major components in the standard are present, and ratio of the peaks in the sample to those in the standard should be consistent within the limitations imposed by the matrix.

11. Quantitation of PCBs as Aroclors

11.1 The quantitation of PCB residues as Aroclors is accomplished by comparison of the sample chromatogram to that of the most similar Aroclor standard. A choice must be made as to which Aroclor is most similar to that of the residue and whether that standard is truly representative of the PCBs in the sample.

11.2 Once the Aroclor pattern has been identified, compare the responses of 5 to 10 major peaks in the single-point calibration standard for that Aroclor with the peaks observed in the sample extract. The amount of Aroclor is calculated using the individual calibration factor for each of the 5 to 10 characteristic peaks chosen in the calibration and the calibration model (linear) established from the multi-point calibration of the 1016/1260 mixture. A concentration is determined using each of the characteristic peaks and then those 5 to 10 closest concentrations of the 5 to 10 concentrations are averaged to determine the concentration of that Aroclor.

11.3 Weathering of PCBs in the environment and changes resulting from waste treatment processes may alter the PCBs to the point that the pattern of a specific Aroclor is no longer recognizable. Samples containing more than one Aroclor present similar problems. The quantitation as Aroclors may be performed by measuring the total area of the PCB pattern and quantitating on the basis of the Aroclor standard that is most similar to the sample. Any peaks that are not identifiable as PCBs on the basis of retention times should be subtracted from the total area. When quantitation is performed in this manner, the problems should be fully described for the data user and the specific procedures employed by the analyst should be thoroughly documented.

12. Data Processing

12.1 The data from the GC run must be reprocessed. This reprocessing includes setting the integration events to draw baselines properly on the chromatogram. In some cases manual integration will be necessary to insure that everything is integrated correctly. Make sure that the data station will calculate the results using average response factors of the 5-point calibration curve.

13. QC Procedure

13.1 Spike information is recorded in the GC instrument logbook

.

13.2 10% of all samples are spiked and spikes are duplicated.

13.3 10% of all samples are duplicated.

13.4 A method blank and a distilled water spike (LCS, QC check) is analyzed with every batch of sample (10 or less sample per batch).

13.5 Surrogate standards are added to all samples before extraction.

13.6 QC charts for all matrixes are updated after each batch of analysis. Corrective actions are taken if any deviation in analysis is observed.

13.7 Solutions from which spiking solutions are made need to be purchased either from a different manufacturer than the one from which Standard solutions are made, or from a different lot# from the same manufacturer. In addition, a 3rd set of solutions should be available, such as ERA or EPA standard solutions. These solutions can be used to check the accuracy of the solutions obtained from other manufacturers.

ENVIRONMENTAL MONITORING DIVISION
HYPERION TREATMENT PLANT – WET CHEMISTRY LABORATORY
STANDARD OPERATING PROCEDURE
For

PARTICLE SIZE DETERMINATION
(Grain Size)
EMD SOP # 4160

Effective Date: 05-02- 2005
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APPROVAL

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TABLE OF CONTENTS

1. SCOPE AND APPLICATION

Ocean and other sediments of size range 0.04 – 2000 um in diameter.

2. SUMMARY OF METHOD

A Coulter LS 230 instrument measures the size distribution of particles from 0.04 um to 2000 um. The instrument with a Fluid Module can measure sample particles suspended in tap water.

The instrument is light scattering particle size analyzer. It uses the diffraction of laser light by particles as the source of information about particle size with diameter 0.4-2000 um. The laser's radiation passes through spatial filter and projection lens to form abeam of light. The beam passes through the sample cell where particles suspended in tap water scatter the incident light in characteristic patterns, which depends on their size. The LS 230 series include another measurement assembly, called PIDS (Polarization Intensity Differential Scattering) . The PIDS provides information for particles in the 0.04-0.4 um range. *A polarized monochromatic light at three different wavelengths: 450, 600, and 900 nm are focused through a slit and are projected the PIDS sample cell.* ***

OR

The sample is placed into the suspension fluid (tap water) in the sample vessel. The suspension fluid and dispersed particles flow through the sample cell. The sample cell stand contains a diffraction sample cell and PIDS sample cell. The Laser beam with a wave 750 um will illuminate the dispersed samples, and a polarized light beam also illuminates the sample. *

3. INTERFERENCES

Gravels (particles larger than 2000 um) interfere. Because, larger particle will obstruct the incident light on the smaller particles and will change the diffraction pattern. Therefore, gravel should be removed and separated from the sample by passing the sample suspension through 2 mm sieve just before adding to the sample vessel. Please note that this separation is a must in order to protect the sensitive sample cell that could scratch. Moreover, the instrument will not measure particles larger than 2000um.

4. SAMPLE COLLECTION, PRESERVATION AND HANDLING

Samples are collected in 8 oz plastic bottles (no preservative is needed by the biologist) and delivered to the EMD sample receiving staff who logs the sample

and informs the Wet Chemistry lab. The samples and store in the sample receiving area refrigerator at 4^0C until analysis have been completed. The samples are saved and kept in the back refrigerator for 1 full year or until the assessment report is completed, which ever is the later. The samples are disposed by the sample receiving staff.

5. EQUIPMENT AND SUPPLIES

Particles size distribution instrument (Coulter Particle Characterization LS230 with fluid Modular) New name is Beckman Coulter Particle Size.

6. CHEMICALS AND REAGENTS : NA

7. SAFETY: Use usual laboratory safety procedures. No special safety precaution is necessary

8. PROCEDURE:

DAILY STARTUP

a. Check on the instrument at the start of each day

Check the water source is turned on.
Check that there is water in the sample vessel. Replace water daily.

Turn on the power switch of the optical Module.
Turn on the printer, the monitor, and the computer.
Check **Use Optical Module** after the LS copy right dialog box appears.
Select **OK.**
Select **Control, Pump On** to turn on the circulating pump.
Select **Control, Rinse** . Let it rinse for about 5 mins then cancel.
Select **Control, Fill**. Wait 2 hours before running a control or sample.
Complete the waiting (warm-up) period.

b. Change Directory or create a new Directory: See Appendix A.

Change to the directory needed for data storage of the next run. Or create separate directories as needed for controls and different types of samples.

c. Load Preferences. See Appendix B.

Load a Preferences file for use with each successive run until you load a different Preference file. Preferences files define how data is presented in the program, how it is printed in reports, what fonts are used, etc. Check page set up to confirm the title and date of your test.

d. Run a Control. Coulter recommends that you run at least one control each day to check instrument performance. Refer to Sample Analysis procedure, and follow any instructions on the assay sheet for the particular control sample. In addition, as the run cycle in progress, make the following checks:

1. Check during offset measuerment that all channels except 127 are less than -/+ 6 mV.

2. Check during alignment that pattern similar to fig 8.7 in the Coulter manual.

3. Check during background measurement that all channels read =/<2X10 6

Sample Preparation:

Sample should be stable, representative of the material sampled. The sample could be wet or dry powder, slurry, and emulsion or dilute suspension.

Sample Amount:

The instrument measures sample amount if you select **Measure Loading** in the Run Cycle dialog box.. This produces a Sample Obscuration screen when it is time to add the sample until the needed obscuration percent appears.
Add about 500 mg of sediment in a shallow weighing dish add a few drops of water. Mix gently with a small spatula. Add the sample as soon as possible after preparation (not before Measuring Loading phase of run cycle).

Sample running instruction

a. Select Cycle in the Run menu and select New Sample. This will automatically select all options. Align should be in Auto mode. Measure Background should be set for 60 seconds and .
b. Load content of the vial during the Measure Loading phase of the cycle into the hopper. Verify that the obscuration is between 5-7%.
c. In Run Info set the run length to 60 seconds and select Compute Sizes and Save File. In Optical Module select Garnet.xxx
d. Select Statistics (Arithmetic's) in the Analyze Menu and verify that the value you obtained are within the limits given by the Vender.

SAMPLE SIZING RUNS

Use this procedure to run new sample and include all instrument functions. Change to the appropriate directory first, so that runs will be saved in the right place.

a. Select **Run, Cycle.**
b. Select **New Sample** (in the dialog box).

c. Change the Run Cycle dialog box as needed.
   1. Check to measure PIDS –range particles.
   2. Change any of the function times as needed. Background time 90 sec.
   3. Select a speed in **Pump Speed** that prevents bubble formation in the suspension fluid yet keeps the control suspended.
   4. Select **Full Speed Rinse** if you reduced the pump speed in the previous step.
   5. Check **Sonicate during loading** to turn on the sonicator while Measure Loading occurs.
   6. Check **Sonicate Before Run** and enter the amount of time before every run in sec.

d. Select **Start.**
e. Wait until the offsets, auto-alignment and background functions are done.
f. When Sample: Obscuration = 0% PIDS = 0% appears on the monitor, add the sample:
   1. Remove the sample vessel lid.
   2. Pour in some prepared sample then stop and watch the screen.
   3. Repeat step b until sample obscuration equals:
      8 to 12% for diffraction only samples.
      45 to 55% for PIDS sample.
   4. Replace the sample vessel lid

.

g. Select **Done.**
h. Fill in the Sample Info dialog box.
   1. Enter a name in **Group ID.** The first eight characters are used as the run file name.
   2. Enter your identifier in **Operator.**
   3. Enter sample identification in **Sample ID**.
   4. Enter a starting run number (01 to 99) in **Run Number** or else the system begins its automatic numbering with 01.
   5. Enter any sample comments in the two Comment text boxes.
   6. Check that the correct suspension fluid appears in the **Fluid** field. If you are going to change suspension fluids:
i. Select **OK**
j. Fill in the Run Info dialog box.
   1. Enter the time duration for the measurement in **Run length.** A diffraction only run needs at least 60 sec. A PID run needs 90 sec.
   2. Enter the time for system to pause between runs in Wait length**.**
   3. Enter the number of runs for this sample in **Number of runs.**
   4. Check **Compute Sizes.**
   5. Check **Save File** if you want run data saved
   6. Check Print Report .
   7. Select Change to change the optical model.

ANALYZE RUN DATA

Compute Size: Use this function to analyze raw data with an optical model or reanalyze data with a different optical model than the one used when the sample was run. See the Manual Chapter 14.4, Make an Optical Model

DAILY SHUTDOWN

Coulter recommends this daily shutdown procedure. If you do not need the instrument for a few days or more, use the Power Down procedure.

a. Perform an Auto Rinse
   1. Select **Run, Cycle.**
   2. Select **Clear All.**
   3. Check **Auto Rinse.**
   4. Select **Start.**
   5. Waite until Auto Rinse: Done appear.

b. Leave fluid in the sample system.
c. Check the drain control is closed.
d. Select **Control, pump Off.**
e. Double click the control menu icon
f. Select **Run, Shutdown Optical Module.**
g. (Optional) Turn off the power switch at the monitor. Turn off the tap water.

POWER DOWN: Coulter recommends that you power down the instrument if it is not to be used for along period of time or as part of service and maintenance

a. Perform an Auto Rinse
   1. Select **Run, Cycle.**
   2. Select **Clear All.**
   3. Check **Auto Rinse.**
   4. Select **Start.**
   5. Wait until Auto Rinse "Done" appears.

b. Leave fluid in the sample system.
c. Check that the drain control is closed.
d. Double click the control menu icon of each open run file, the main window of the LS program and the Program Manager window.
e. Select **OK** when this will end your Windows session appears. Turn off the power switches at the Optical Module, monitor, printer and computer.
f. Turn off the tap water at it source.

Create a Directory

To create a new directory for run data storage:

a. Perform change the directory procedure to display the path name needed for the new directory. e.g. c|:\windows\ls.
b. Select **File**, **Create Directory**.
c. Enter the name of the new directory. Use up to eight characters to name a directory file.
d. Select **Create.**
e. Use the Change Directory procedure to make this the active directory.

Change the Directory

Use this function to change the directory where you want the next run's data to be stored.

a. Select **File**, **Change Directory**.
b. Select the directory name in the list box
c. Select **Change** and the directory 's name appear in the path name. See Figure 8.5.
d. Select **OK** to change to this directory.

Load a Preferences File

If you just powered up, the current Preference file is the DEFAULT.PRF file.

a. Select **Preference**, **Load Preferences**.
b. Check the path name. Select the name of the directory of the needed Preferences file if it is different than the one displayed in the path name. Select Open .
d. Select the name of the Preferences file to highlight it.
e. Select Open**. This Preference file is used for all samples run until you load a different Preference file or power off.**

9. DOCUMENTATION & CALCULATION:
Open the Excel worksheet for Grain Size. Enter sample dates and the rest of the information. Enter corresponding data for each sample from the instrument's print out. .

10. DATA MANAGEMENT: **Print out the Excel report sheet, have it checked and file.**

11. QUALITY ASSURANCE AND QUALITY CONTROL
Run two daily control standards before analyzing the samples

Passing Criteria:

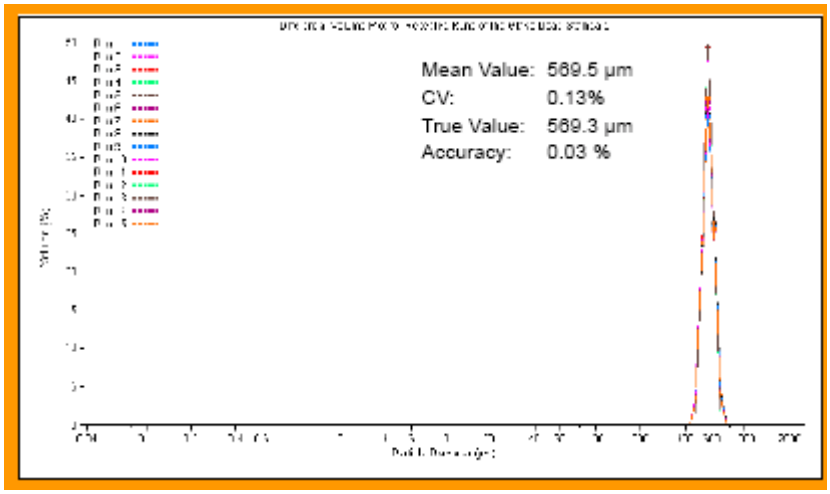
Control Name: GB 500 Mean= 546.35 +/- 34.5 um Std. Dev= 57.54 +/- 22.5 um
Control Name: GB 35 Mean = 34 +/- 1.5 um Std. Dev. = 13.3 +/- 2.5 um

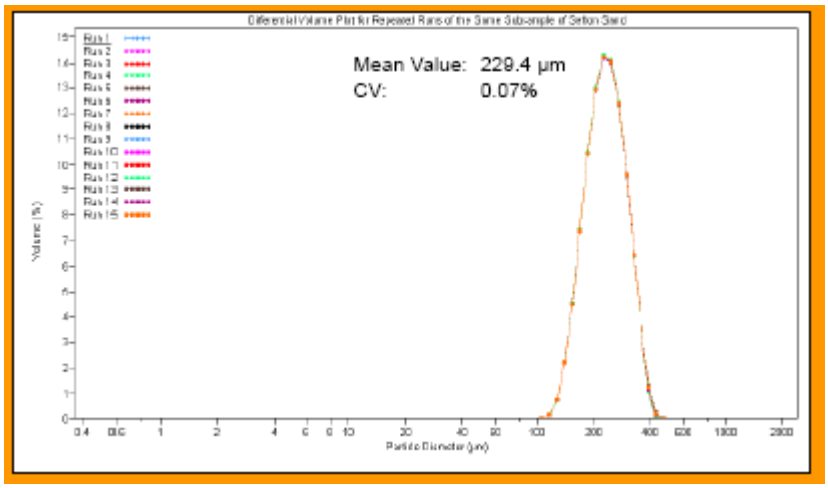
12. REPORTING LEVEL: **Particle sizes 0.04µ to 2000µ**

13. PRECISION AND BIAS STATEMENT

The accuracy of the instrument is regularly checked by way of internal calibration and a proficiency testing scheme which compares results from a group of laboratories three times a year. Repeated internal testing with a certified glass bead control standard has demonstrated an accuracy of 0.03 % for the mean grain size when compared to the true value.

Instrument precision has been assessed through 15 repeated runs of the same sub sample of both the glass bead control standard and a well sorted dune sand from the Sefton coast, UK. The coefficient of variation (CV) for the mean grain size of these runs was 0.13 % and 0.07 % respectively.





Differential volume plots for repeated runs of the glass bead standard (top) and Sefton sand (lower)

14. REFERENCES

- Coulter Product Manual, LS Series- LS 230, issue A, May 1994

Alderliestern, M:1984. A Nomenclature For Mean Particle Diameters,

Analytical Proceedings, Vol. 21, May 1984, Royal Society of Chemistry, London, England.

Godfrey NB: 1972. Chemical Technology (20 359.

Hildebrand Jhand /scott RL:1950. The Solubility of Nonelectrolytes.

Reinhold Publishing Corp., New York NY.

Irani RR and Callis CF:1963. Particle Size: Measurements, Interpretation, and Application. John Wiley and Sons, Inc., New York-London.

Manufacturing Chemists, Association: 1972. Te Guide for Safety in the Chemical Laboratory. Van Nostrand Reinhold Company, New York, NY, USA

Sax N:1969. Dangerous Properties of Industrial Materials. Van Nostrand Reinhold Company, New York, NY, USA

Weast RC:1962. CRC Handbook of Chemistry and Physics. CRC Press Inc.,

West Palm Beach, FL.

Windholz M:1989. The Merck Index, 11th Edition. Merck & Co., Inc., Rahway, NJ, USA

15. APPENDICES

Appendix A: **To change the directory, go to the program manager, select the appropriate directory for the samples and click "Change Directory", OK and Exit.**

If there is no related directory for the samples and you need to create one, go to program manager, click file, new, new directory, give a name to this new directory and click ok.

Appendix B: **In Coulter LX main screen top menu, go to "Preferences" and click on "Load Preferences", find the appropriate preference file in the related directory and click "OK".**

Note: You can edit the Preference file according to your needs using the functions located in the "Preferences" menu item and save it for future needs using " Save Directory" command.

ENVIRONMENTAL MONITORING DIVISION
HYPERION TREATMENT PLANT - WET CHEMISTRY LABORATORY
STANDARD OPERATING PROCEDURE
For

TOC-Solid

5310B SM 20th Edition
EMD SOP# 4151
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Effective Date: 09-09-05
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Total Number of Pages: 8

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TABLE OF CONTENTS

I. Scope and Application

This method is used in the analysis of water, wastewater, domestic and industrial wastes, sediments

II. Summary of Method

Sample is homogenized and treated with acid to remove inorganic carbon. The treated sample is introduced into a heated reaction chamber. A continuous flow of oxygen or air is passed through the chamber, which is equipped with a Co catalyst. Through catalytic oxidation, the sample is completely oxidized to CO_2 and H_2O. The CO_2 product stream is passed through a halogen trap then moisture trap. CO_2 concentration is measured by NDIR, a non-dispersive infrared detector. The obtained result represents the total organic carbon (TOC) content of the solid sample.

III. Interferences

Solid samples have particles of different sizes; therefore, it is difficult to achieve sample homogeneity

IV. Sample Collection, Preservation and Handling

Sample is collected in a glass 100mL container. Holding time is 28days

V. **Apparatus** (Shimadzu TOC-Vws)

The Boat Sampling Module contains two sample introduction ports for maximum flexibility. There is a flip-top hatch which is used for solids and other samples which cannot be drawn up into an ordinary syringe.

During analyses, the boat resides in closed system which is flushed continuously with 200 cc/min of oxygen. The user manually advances the boat containing treated sample into the furnace. There, the sample is vaporized and swept by the continuous oxygen flow to the 800 c combustion zone where all carbonaceous matter is oxidized to CO2 .The carbon dioxide is bubbled through an acidified liquid and then routed through a mist trap which together serve to remove any entrained water and scrub out an corrosive species formed.

Finally, the gas is swept to the linearized non-dispersive infrared detector which is made specific for CO2, measurement. The Electronics/Control Module integrated the detector signal and displays the analysis result in ppmC concentration units.

Glassware Placement:

1. Fit a solid grey septum in the side port located about midway along the body of the pyrex sparger, and a solid red/white septum at the bottom.

2. Using a squirt bottle, fill the sparqer with deionized water until the white disperser/frit at the bottom is well submerged. Acidify the water with a couple of drops of phosphoric acid, to pH =2

3. Place a red septa connector w/ TEFLON backing in each of the two remaining ports of the sparger.

4. Install the sparger in the middle position of the grey PVC sparger stand.

5. Place one red septa connector w/ TEFLON backing in each of the two ports of the pyrex mist trap.

6. Install the mist trap in the left most position of the PVC sparger stand.

7. Connect the side tilted port of the sparger to the upright port of the mist trap with an 8" length of 1/8 " Teflon tubing.

Inlet Race Tube Assembly

1. From the right side of the hatch block, remove the square o-ring clamp.

2. Verify the presence of an o-ring at the inside rim of the exposed hole.

3. Install the pyrex inlet race tube in the clips at the far right end of the top panel such-that its side port is to the left and is positioned upright.

4. Place the square o-ring clamp over the left end of the pyrex race tube.

5. Permanently position the race tube by positioning it in the hatch block as far as it will go and reinstalling the o-ring clamp removed earlier.

6. Locate the push-rod assembly and a platinum sample boat Seat the boat in the cradle at the end of the push-rod assembly.

7. Insert the push-rod boat assembly (boat end first) through the open right end of the pyrex race tube. Caution against bending the wire.

8. Set the large u-magnet , flat sides up, underneath the magnetic coupler of the pushrod assembly.

9. Straddle the 2 magnetic field extenders in parallel fashion over the pyrex race tube to connect like poles of the large magnet.

10. Lift the hatch. Slowly move the magnetic coupling to position the sample boat directly under the hatch port.

11. Install a solid red/white Teflon-backed septum in the side port of the race tube.

12. Connect a 118" Teflon gas line from the 200 cc/min flow restrictor (along inside top of right panel, marked with a blue dot) to the far right end of the pyrex race tube. Secure the tubing-in place with grey holed septum .

Combustion Tube Packing & Installation

1. Verify again that the Boat Sampling Module is powered down. Its parts should be at or near room temperature for safe and comfortable handling.

2. Locate the dimple in the quartz combustion tube . Feed a tuft of quartz wool in through the opposite end until it reaches the dimple.

3. Through the open end, insert about 2 inches of cobalt oxide catalyst . Gently tap the tube against a bench top several times to ensure uniform packing of the cobalt oxide.

4. Secure the cobalt oxide in place with a second tuft of quartz wool.

5. Remove the larger bolt on the left side of the hatch block.

   Verify that two o-rings are present are present in the plate from which the bolt was removed. if not remove the plate. Set one o-ring along the inside rim of the big hatch block. Set the other at the far end of the plate facing the hatch block.

6. Slide the packed combustion tube in through the hole in the left panel of the Boat Sampling Module until it emerges about 114" from the right panel.

7. Fit the unthreaded portion of the 112" bolt around the combustion tube. Reattach the bolt to the hatch plate.

Gas Plumbing:

1. install a 118" Teflon or copper (air-conditioning) line from the two-stage regulator on the gas.--cylinder to the brass bulkhead, labeled “O2” in on the rear panel of the Boat Sampling.Module.

2. Pack the tin/copper Sn/Cu, scrubber:

   Fit one end of a pyrex scrubber tube with a cored grey septum. Insert a tuft of pyrex wool and then about 2 inches o&20-mesh tin in the other end. Secure the

tin with another tuft of pyrex wool. Then, fill the remaining half of the scrubber tube with an equal amount of copper. Secure the copper with a third tuft of pyrex wool. Install a cored grey septum at the end.

3. Connect the Sn/Cu scrub to the permeation dryer of the Electronics/Control Module using 1/8" OD Teflon tubing.

4. Connect the free end of the Sn/Cu scrubber to the side port of the mist trap. Step down tubing consisting of a length of 1/8" OD Teflon tubing fitted over a length of 1/16" Teflon tubing may be necessary.

5. At the exit end of the combustion tube, install a 1/8" OD Teflon tube fitted with a cored grey septum . Connect the opposite end to the top of the pyrex sparger.
6. Connect a piece of 1/16" OD Teflon tubing between the side port of the sparger and the top port of the mist trap.

   If the range extension kit is included, refer to instructions provided with the kit for additional information on gas plumbing.

7. The Teflon line emerging from the right hole above the PVC sparger stand is used with the external sparging station only (right-hand station of the sparger stand). Following sample acidification, this line will <u>deliver 50 cc/min</u> to the sample for the elimination of inorganic carbon.

3. <u>Condition the catalyst:</u>
   Conditioning the catalyst helps trap any toxic fumes which may be released by the cobalt oxide during its initial heating.
   Exercise caution when handling parts. if necessary, wait until heated components have cooled.

a. Power down the Boat Sampling Module.

b. Disconnect the Teflon line and septum at the exit end of the combustion tube. In its place, install a 15" length of 1/8" OD Teflon tubing fitted with cored grey septum.

c. Insert the free end of the new Teflon line into a flask containing basic sodium hydroxide solution.

d. Flip the toggle between the sparger and the mist trap to the up position. Observe the brisk bubbling of gas through the flask (at about 200 cc/min).

e. Power up the Boat Sampling Module again. Allow the furnace to become hot.

f. Allow the cobalt oxide to condition in this manner for about 1 hour.

g. Power down the furnace to facilitate-the removal of the Teflon line installed in step b.

h. Power up the Boat Sampling Module again.

4. Calibrate the system using a 40 ul injection of 1000ppm, 5000ppm, 10000ppm, 15000ppm KHP standards. Refer to the basic system manual for specific instructions on calibrating.

VI. Chemical and Reagent

TOC-SOLID standards
Prepare a 25000 ppmC standard stock solution by using reagent grade potassium hydrogen phthalate in reagent water in a 500 ml volumetric flask. Add 0.1 ml of concentrated nitric acid, and make to volume with reagent water. Store the stock in refrigeration. Replace the stock monthly.
From stock solution prepare 1000ppm, 5000ppm, 7500ppm, 10000ppm, 15000ppm standards. Use 5000ppm as the spike solution.
From different stock solution, prepare QC standard.

VII. Safety

Conditioning the catalyst helps trap any toxic fumes, which may be released by the cobalt oxide during its initial heating.
Exercise caution when handling parts. If necessary, wait until heated components have cooled.

VIII. Procedure

IC removal

Mix sediment thoroughly with a metal spatula
Load sample onto a clean boat, weigh about 10 to 50 mg depending on the sample type using analytical balance, record the weight.
Add 2 drops of (1+1) HNO3 to convert the carbonate form to CO2.
Put under an IR lamp, about 10 minutes (for the completion of the reaction); check the completeness of the inorganic carbon removal by adding 1 or 2 drops of (1+1) HNO3 (until no CO2 bubble is observed).

Operation

(Follow TOC Talk for 183 Boat Analysis)

Flip the left toggle switch (above the sparger stand) to the up position. Observe the brisk bubbling as through the pyrex sparger. The regulator on the gas cylinder should show a steady delivery of oxygen at 30 psig.

After 15 minutes or so 6 the furnace temperature should be stable at about 800 C. At this temperature, the quartz combustion tube will have a characteristic orange glow and the green LED on the front panel becomes lit. To verify the temperature, follow the appropriate step given above under "Initial Start-up," step #2.-

(A yellow glow would indicate the furnace far exceeds this temperature. When the furnace is "over-temperature", the red LED on the front panel lights to alert the user that the Module should be serviced.
With the Boat Sampling Module at full operating temperature, advance the platinum sample boat into the furnace. Allow the boat to bake there for about 2 minutes. Then, retract the boat so that it resides again in the hatch block.

6. At the beginning of an analysis day, place a new tuft of quartz wool in the sample boat. Whenever the wool is replaced, bake the boat as described in step 4 above.

   The quartz wool helps promote even vaporization of sample from the boat while in the furnace.

7. Monitor the baseline. Verify that it is stable.

c. Lift the hatch. Situate the sample boat under the hatch port

d. Close the hatch. Allow the detector baseline to stabilize (wait 1-2 minutes).

e. Press START and advance the boat into the furnace at about 2 inches (5 cm) per second.

   Respond to all screen queries, then wait for the "inject now" screen message before advancing the boat into the furnace.

f. Wait 2-8 minutes for the analysis to finish

g. Retract the boat back to the hatch port. Allow the boat to cool for about 30 seconds before introducing the next sample.

IX. Calculation

a) The analyzer automatically calculates results.
b) Enter the average raw data into the excel worksheet for 6 calibration point curve.
c) Enter the average raw data into Excel worksheet for all samples, QC, and Spike.

e) Evaluate the results.
f) Check data entry.
g) Enter data to the report spreadsheet or/and LIMS.

X. Data Management

The analyst is responsible for assuring compliance with QA-QC requirements. The supervisor is notified when results are out of range. Analysis is repeated to confirm outliers.

XI. Quality Assurance and Quality Control

A set of duplicate spiked samples is analyzed for every batch of 10 samples. The relative percent difference (RPD) should be less than 25%. The spike recovery should be 100-+25%.

XII. Lowest Reporting Level

The lowest reporting level is 50 mg C/L.

XIII. Precision and Bias Statement

XIV. References

a) Standard Methods, 18th Ed., 5310 B page 5-11 to 5-13.
b) Apollo 9000 TOC Combustion Analyzer User Manual
c) Installation and Operation of the 183 Boat Sampling Module with Apollo 9000

XV. Appendices

APPENDIX G

Data Acquisition, Reduction, Validation, and Reporting SOPs

When performing analyses, results are generally tabulated onto laboratory worksheets but sometimes are generated electronically via instrumentation. Data on laboratory worksheets are entered into the Laboratory Information Management System using an Excel interface. These data are then validated through a quality assurance process that checks for correctness of data entry and validity of results. The analyst who generates the data has the initial and primary responsibility for the completeness and correctness of the data. The data are then checked by the unit supervisor (or designee). The following procedures describe the data acquisition and entry process then the quality assurance and quality control procedures.

Data Acquisition

Both raw and calculated data are acquired in the laboratory by manual, electronic, or direct computer acquisition. Acquired data are properly and securely stored for the duration specified by regulatory agencies or the customer. Guidelines for documentation and recording of information are as follows:

- Manual (Hand-written) Data Entry
    - Data are entered directly into the notebook or worksheet with non-erasable ink.
    - Data entries are signed and dated by the analyst making the entry. If the entry is more than one page, each page is signed and dated.
    - Mistakes are canceled by drawing a line through the entry, entering the correct value, and signing and dating the correction. The use of correction fluid is not acceptable.
    - Blank pages or substantial portions of pages with no entries are marked with a large "X" to indicate that they were intentionally left blank.

- Direct Computer Acquisition
    - In EMD, the program/software used to generate results is prepared internally. A designated staff member of the Information & Control System Division (ICSD) at Hyperion has the responsibility of preparing the program and maintaining the supporting documents.
    - The laboratory relies on vendor-supplied information for the validity and integrity of instruments equipped with significant computer functions as an integral part of the system.

Data Reduction

Data reduction, where applicable, is described in specific SOP's. It involves reporting values with the appropriate significant figures in the concentration units established by the regulatory agency or the data user.

Review and Validation

Review

Data review is the process of comparing results to all available information, such as sample preparation and QC sample data, to evaluate the validity of the results. It supports the contention that the data are:

- Reasonable (experience with similar situations, common sense), and
- Capable of supporting a defensible decision.

The analyst and the unit supervisor (or designee) are responsible for reviewing the data relative to the following:

- Method blanks and QC sample
- Raw data
- Calculations
- Transcription

Validation

Data validation is the systematic procedure of reviewing data against a set of criteria to provide assurance of its validity before reporting the data. It is accomplished through routine examination of data collection, flow procedures, and QC sample results. It uses QC criteria to reject or accept specific data.

- Validation includes the following:
  - Dated and signed entries by analysts on the worksheets and logbooks used for all samples.
  - Use of QC criteria to reject or accept specific data.
  - Checking of LIMS data entry and reporting
- Validation Guidelines include the following:
  - Documentation of methods used and QC applied.
  - Maintenance performed on instruments.
  - Documentation of sample preservation, transport, and storage.
  - Review of QC sample data.

Data validation is performed, signed, and dated by the analyst, the unit supervisor (or designee), and where applicable, the laboratory manager.

Reporting

Data prepared for release to the Legal Reporting Unit are checked and approved by the unit supervisor (or designee) by the 5th of the following month for the previous month's data. The final report is prepared by the Legal Reporting Unit of EMD. The report is again scanned for missing data and outliers. Regulatory limitation calculations will be applied to the data set and exceedances clearly listed. If stations are out-of-compliance, accelerated monitoring will be indicated. Any regulatory required summary reports of source identification findings or sanitary surveys will be included. The report is signed by the Division Manager before distribution and may include the following:

- Sample ID used by the laboratory and the client (if available).
- Sample matrix type, description, and method number.
- The chemical/physical/biological parameters analyzed with the reported values and units of measurement.
- Data for all parameters reported with consistent number of significant figures.
- Results of QC samples, if appropriate.
- Footnotes referenced to specific data, if required, to explain reported values.
- If there are regulatory limits applicable to specific analyses, then limits are clearly notated and exceedances listed.
- Discussion on non-compliance data
- Report transmittal letter or memorandum identifying the person sending the report and the person(s) receiving the data.

APPENDIX H

Quality Assurance/Quality Control

The quality assurance objectives for measurement of data are unique to the particular program for which the data are collected and utilized. They describe the overall uncertainty that the data user is willing to accept in order to make decisions for environmental or other concerns. This uncertainty describes the data quality that is needed, which are usually expressed in terms of precision, bias, representativeness, comparability, and completeness.

The participating laboratories will use approved and recognized test methods, and comply with uncertainty requirements of the method. Quality control samples are measured and uncertainties are assessed and results must be within the range prescribed by the methods. Internal acceptance criteria are established by analyzing laboratory control samples on a daily basis. The participating laboratories will strive to meet the QA/QC goals described in this section and, therefore, be able to attest to the integrity of the sampling and analytical process.

The following QA/QC procedures will be conducted for shoreline sample collection, laboratory analyses, and data management to ensure the production of reliable and defensible data.

Sample Collection

Only trained laboratory staff will be assigned to collect samples using proper sampling procedures, appropriate sampling equipment, required containers, and proper preservation techniques.

General guidelines for sample collection by laboratory staff are as follows:

- Label sample containers with sample date, sample time, sampling point, sample type (grab/composite), preservatives added (if needed), the name of the sampler, and analyses needed.
- Use aseptic technique when collecting samples to prevent contamination.
- Avoid collecting sample in multiple sweeps and no refilling of the sample bottle.
- Once the sample is collected, immerse at least one-third of the sample bottle in ice.
- Once received, log the samples into the laboratory system as soon as possible, assign a unique login number, and properly store.
- Sample preparation steps done prior to analysis, such as sample preservation are described in individual test SOP's.

Sample Handling

Chain-of-Custody

The purpose of the chain-of-custody is to establish detailed written and legal documentation of all transactions in which samples are transferred from the custody of one individual to another. The custody procedure is also used whenever samples are

submitted to a laboratory within the division or to a contract laboratory. The chain-of-custody begins at the sample collection site and includes couriers or messengers who handle the sample in transit. It follows the sample in the laboratory until its ultimate disposal. It is a form of proof used to establish the authenticity and integrity of the sample, since the results will be used to show compliance with the TMDL requirements, i.e., numeric targets and wasteload allocations.

A Chain-of-Custody (COC) must accompany each sample submitted to a participating laboratory. If a COC has not been filled out prior to delivery of the sample, a form will be provided to the delivery person prior to acceptance of said sample. The COC will be reviewed to make sure that all of the needed information has been supplied. As an example, the Chain-of-Custody Form being used at EMD is attached (Appendix E).

Sample Holding & Preservation

Samples must meet EPA holding time requirements for each testing parameter.

After the sample is received, the participating laboratory will enter the sample information into the Laboratory Information Management System (LIMS) or comparable database and a unique laboratory registration number will be generated for that sample.

Sample Disposal

After the analyses are completed the sample will be retained as legal evidence or legally disposed. Analyzed samples and standards used in analyses are disposed of in accordance with the laboratories written procedures, e.g., EMD's Chemical Hygiene Plan.

Analytical Procedures

Analyses

Analyses performed at EMD laboratories are generally driven by regulatory concerns and plant operations' requirements. There are many different analytical methods applicable to environmental analyses. EMD's methods are generally based on those specified by Federal and State regulatory agencies or professional organizations. As a guide, references for the analytical procedures are listed below.

"Standard Methods for the Examination of Water and Wastewater", 18^{th} – 20^{th} edition, 1992 and 1998 respectively, APHA, AWWA, WPCF, Washington, DC.

"Methods for Chemical Analysis of Water and Wastes", EPA-600/4-79-020, revised March 1983.

Test Methods for Evaluating Solid Waste. 1986. Revision December 4, 1996. Volume IB: Laboratory Manual Physical/Chemical Methods, 3rd Edition. United States Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, D.C.

Standard Operating Procedures (SOPs)

Routine analyses are defined in Standard Operating Procedures (SOPs), which are detailed descriptions of how to use and what to expect from a method. They contain method-specific QC criteria (i.e., instrument calibration, reagent blank, method blank, calibration standards, etc.), and QC requirements such as duplicate analysis, spike recoveries, holding time, etc. EMD follows a standardized SOP format, its content and application is presented in Appendix F of this document.

System and Performance Audits

An audit is a periodic check to ensure that the laboratory operates according to the policies and procedures described in the Quality Assurance Manual, complies with good laboratory practices, and meets the requirements of regulatory agencies. It may be either a system or performance audit.

System Audit

A system audit is a review of laboratory operations conducted to verify that the laboratory has the necessary facilities, equipment, staff, and procedures in place to generate acceptable data. It is an on-site inspection of the laboratory's system of operations. It may be an internal or external audit. Internal inspections may be performed by quality assurance personnel. External audits are generally laboratory certification-related activities.

1. Internal

   Periodically, the QA Officer (or designee) audits the laboratories and reports the results to the Division Manager (or laboratory director), laboratory managers, and unit supervisors.

2. External

   State-certified laboratories are site visited every two years by auditors from the Environmental Laboratory Accreditation Program (ELAP) of the California Department of Health Services (CA DOHS). Accreditation is by scientific discipline or field of testing. Non-compliances with good laboratory practices are identified and reported as deficiencies and are subject to corrective action before accreditation is renewed.

Performance Audit

A performance audit is a review to evaluate the laboratory's analytical activities as well as the data produced by analysts. It verifies the ability of the laboratory to correctly identify and quantify compounds in unknown samples submitted by the auditing entity. The purpose of these audits is to determine the laboratory's capability to generate scientifically sound data.

1. Internal

   Periodically, the QA staff submits unknown samples to most of the laboratories. These samples are usually from the inventory of previous Performance Evaluation (PE) samples from EPA. Analysis of these samples is also a corrective action requirement for Discharge Monitoring Report (DMR) and/or Water Pollution (WP) samples evaluated with "unacceptable results". The QA staff may also conduct intra- and inter-comparison studies.

2. External

   All laboratory units, including the Microbiology laboratory, at EMD participate in mandatory QA Performance Evaluation (PE) Study Programs.

   a. Mandatory PE Programs

      * Water Pollution QA Study Program (WP) serves a dual purpose. It satisfies EPA's wastewater testing laboratory requirements and meets one of ELAP's certification criteria. Test samples are analyzed for parameters listed under each field of testing on our certifications and are specified in the WP Program following certified procedures. A laboratory can participate in a WP Study twice a year.

      * For the Microbiology Performance Evaluation (PE) Study, Drinking Water/Wastewater Enumeration is required for ELAP certification. Like all the other PE programs, the samples are acquired from NIST-approved vendors and analyses are done for certified analytes.

   b. Voluntary PE Program

      The Microbiology Unit also takes part in the interlaboratory calibration studies with EPA. These programs are performance based.

Assessment of Precision and Accuracy

Data quality may be assessed in terms of precision, accuracy, representativeness, completeness, and comparability. The latter three are usually determined outside of the laboratory operations and with limited involvement of laboratory staff. These measures are

not included in this section. The internal quality control measures (i.e., precision and accuracy) that are performed in the laboratory to evaluate data quality are described in this section.

Precision

Precision is the agreement among a set of replicate measurements without knowledge of the true value. It is the degree to which a measurement is reproducible. Precision, expressed as Relative Percent Difference (RPD), is determined for each laboratory unit by analyzing replicates of the same sample, a number of duplicate pairs, or matrix-spiked duplicate samples.

Accuracy

Accuracy is a measurement of how close the result is to the true value. Each laboratory unit establishes its accuracy of measurement by analyzing QC check samples (spiked samples, standard reference materials from a reliable source, etc). The results of the QC samples are correlated to documented, certified values. Results of spiked samples are calculated as Percent Recovery. Actual Percent Recovery is compared to established reference data. The degree of closeness of the QC check sample contributes to the general assurance that the accuracy of the data is within acceptable limits.

Corrective Action

Laboratory events and data that fall outside established quality acceptance criteria may require investigation or corrective action. The corrective action implemented depends on the type of analysis, the extent of the error, and whether the error can be determined and corrected. The purpose of the corrective action is to resolve the problem and to restore the system to proper operation. Investigative steps and corrective actions implemented are documented.

Corrective Action Procedures

1. The initial corrective action procedures may be handled at the bench level. The unit supervisor is immediately notified of the deviation. The analyst reviews the sample preparation for possible errors and checks the instrument calibration, calibration and spike solutions, instrument sensitivity, etc.

2. If the error cannot be resolved by the analyst, the unit supervisor has the responsibility of resolving the problem with assistance, if needed, from the laboratory manager and/or the QA Officer.

3. The corrective action adopted may be determined by the analyst, the unit supervisor, the laboratory manager, the QA Officer, or through a consensus. If needed, the final decision for corrective action rests with the laboratory manager after consultation with the QA Officer.

4. The unit supervisor shall maintain an accurate and up-to-date record of corrective actions taken in the unit. A corrective action report form (included herein as an attachment) is available for use.

5. The laboratory manager shall periodically review corrective action records and plan for system improvement by involving analysts, unit supervisors, and QA personnel.

General Guidelines for Initiating a Corrective Action

1. Identify/define the problem.
2. Assign responsibility for investigating the problem.
3. Investigate and determine the causes.
4. Develop corrective action to eliminate the problem.
5. Measure the effectiveness of the corrective action.
6. Analyst, unit supervisor, laboratory manager, and the QA Officer meet to review and evaluate the process, if necessary.
7. Document the process by filling out the Corrective Action Report Form.

APPENDIX I

Regional Board Resolution No R05-007 for Ballona Creek Metals TMDL

Attachment A to Resolution No. R05-007

Amendment to the Water Quality Control Plan – Los Angeles Region to incorporate the Ballona Creek Metals TMDL

Adopted by the California Regional Water Quality Control Board, Los Angeles Region on July 7, 2005.

Amendments:

Table of Contents
Add:

Chapter 7. Total Maximum Daily Loads (TMDLs) Summaries
7-12 Ballona Creek Metals TMDL

List of Figures, Tables and Inserts
Add:

Chapter 7. Total Maximum Daily Loads (TMDLs)
Tables
7-12 Ballona Creek Metals TMDL
7-12.1. Ballona Creek Metals TMDL: Elements
7-12.2. Ballona Creek Metals TMDL: Implementation Schedule

Chapter 7. Total Maximum Daily Loads (TMDLs) Summaries, Section 7-12 (Ballona Creek Metals TMDL)
Add:

This TMDL was adopted by the Regional Water Quality Control Board on July 7, 2005.

This TMDL was approved by:

The State Water Resources Control Board on [Insert Date].
The Office of Administrative Law on [Insert Date].
The U.S. Environmental Protection Agency on [Insert Date].

The following tables include the elements of this TMDL.

Table 7-12.1. Ballona Creek and Ballona Creek Estuary Metals TMDL: Elements

Element	Key Findings and Regulatory Provisions
Problem Statement	Ballona Creek is on Clean Water Act Section 303(d) list of impaired waterbodies for dissolved copper, dissolved lead, total selenium, and dissolved zinc and Sepulveda Canyon Channel is 303(d) listed for lead. The metals subject to this TMDL are toxic pollutants, and the existing water quality objectives for the metals reflect national policy that the discharge of toxic pollutants in toxic amounts be prohibited. When one of the metals subject to this TMDL is present at levels exceeding the existing numeric objectives, then the receiving water is toxic. The following designated beneficial uses are impaired by these metals: water contact recreation (REC1); non-contact water recreation (REC2); warm freshwater habitat (WARM); estuarine habitat (EST); marine habitat (MAR); wildlife habitat (WILD); rare and threatened or endangered species (RARE); migration of aquatic organisms (MIGR); reproduction and early development of fish (SPWN); commercial and sport fishing (COMM); and shellfish harvesting (SHELL). TMDLs are developed for reaches on the 303(d) list and metal allocations are developed for tributaries that drain to impaired reaches. This TMDL address dry- and wet-weather discharges of copper, lead, selenium and zinc in Ballona Creek and Sepulveda Canyon Channel.
Numeric Target *(Interpretation of the narrative and numeric water quality objective, used to calculate the load allocations)*	Numeric water quality targets are based on the numeric water quality standards established for metals by the California Toxics Rule (CTR). The targets are expressed in terms of total recoverable metals. There are separate numeric targets for dry and wet weather because hardness values and flow conditions in Ballona Creek and Sepulveda Canyon Channel vary between dry and wet weather. The dry-weather targets apply to days when the maximum daily flow in Ballona Creek is less than 40 cubic feet per second (cfs). The wet-weather targets apply to days when the maximum daily flow in Ballona Creek is equal to or greater than 40 cfs. **Dry Weather** The dry-weather targets are based on the chronic CTR criteria. The copper, lead and zinc targets are dependent on hardness to adjust for site-specific conditions and require conversion factors to convert between dissolved and total recoverable metals. These targets are based on the 50th percentile hardness value of 300 mg/L and the CTR default conversion factors. The conversion factor for lead is hardness dependent, which is also based on a hardness of 300 mg/L. The dry-weather target for selenium is independent of hardness and expressed as total recoverable metals. **Dry-weather numeric targets (µg total recoverable metals/L)** Copper: Dissolved 23, Conversion Factor 0.96, Total Recoverable 24 Lead: Dissolved 8.1, Conversion Factor 0.631, Total Recoverable 13 Selenium: Total Recoverable 5 Zinc: Dissolved 300, Conversion Factor 0.986, Total Recoverable 304

Element	Key Findings and Regulatory Provisions
	Wet Weather The wet-weather targets for copper, lead and zinc are based on the acute CTR criteria and the 50th percentile hardness value of 77 mg/L for storm water collected at Sawtelle Boulevard. Conversion factors for copper and zinc are based on a regression of dissolved metal values to total metal values collected at Sawtelle. The CTR default conversion factor based on a hardness value of 77 mg/L is used for lead. The wet-weather target for selenium is independent of hardness and expressed as total recoverable metals. **Wet-weather numeric targets (ug total recoverable metals/L)** Copper: Dissolved 11, Conversion Factor 0.62, Total Recoverable 18 Lead: Dissolved 49, Conversion Factor 0.829, Total Recoverable 59 Selenium: Total Recoverable 5 Zinc: Dissolved 94, Conversion Factor 0.79, Total Recoverable 119
Source Analysis	There are significant difference in the sources of copper, lead, selenium and zinc loadings during dry weather and wet weather. During dry weather, most of the metals loadings are in the dissolved form. Storm drains convey a large percentage of the metals loadings during dry weather because although their flows are typically low, concentrations of metals in urban runoff may be quite high. During dry years, dry-weather loadings account for 25-35% of the annual metals loadings. Additional sources of dry weather flow and metals loading include groundwater discharge and flows from other permitted NPDES discharges within the watershed. During wet weather, most of the metals loadings in Ballona Creek are in the particulate form and are associated with wet-weather storm water flows. On an annual basis, storm water contributes about 91% of the copper loading and 92% of the lead loading to Ballona Creek. Storm water flow is permitted through the municipal separate storm sewer system (MS4) permit issued to the County of Los Angeles, a separate Caltrans storm water permit, a general construction storm water permit, and a general industrial storm water permit. Non-point sources are not considered to be a significant source in this TMDL. Direct atmospheric deposition of metals is insignificant relative to the annual dry-weather loading or the total annual loading. Indirect atmospheric deposition reflects the process by which metals deposited on the land surface may be washed off during storm events and delivered to Ballona Creek and its tributaries. The loading of metals associated with indirect atmospheric deposition are accounted for in the estimates of the storm water loading.

<table>
<tr><th>Element</th><th>Key Findings and Regulatory Provisions</th></tr>
<tr><td>Loading Capacity</td><td>TMDLs are developed for copper, lead, selenium and zinc for Ballona Creek and Sepulveda Canyon Channel.

Dry Weather

Dry-weather loading capacities for Ballona Creek and Sepulveda Canyon Channel are equal to the dry-weather numeric targets multiplied by the critical dry-weather flow for each waterbody. Based on long-term flow records for Ballona Creek at Sawtelle the median dry-weather flow is 14 cfs. The median dry-weather flow for Sepulveda Canyon Channel, based on measurements conducted in 2003, is 6.3 cfs.

<u>Dry-weather loading capacity (grams total recoverable metals/day)</u>
<table><tr><th></th><th>Copper</th><th>Lead</th><th>Selenium</th><th>Zinc</th></tr><tr><td>Ballona Creek</td><td>821</td><td>440</td><td>171</td><td>10,423</td></tr><tr><td>Sepulveda Channel</td><td>371</td><td>199</td><td>77</td><td>4,712</td></tr></table>
Wet Weather

Wet-weather loading capacities are calculated by multiplying the daily storm volume by the wet-weather numeric target for each metal.

<u>Wet-weather loading capacity (total recoverable metals)</u>
<table><tr><th>Metal</th><th>Load Capacity</th></tr><tr><td>Copper</td><td>Daily storm volume x 18 µg/L</td></tr><tr><td>Lead</td><td>Daily storm volume x 59 µg/L</td></tr><tr><td>Selenium</td><td>Daily storm volume x 5 µg/L</td></tr><tr><td>Zinc</td><td>Daily storm volume x 119 µg/L</td></tr></table></td></tr>
<tr><td>Load Allocations (for nonpoint sources)</td><td>Load allocations (LA) are assigned to non-point sources for Ballona Creek and Sepulveda Canyon Channel.

Dry Weather

Dry-weather load allocations for copper, lead and zinc are developed for direct atmospheric deposition. The mass-based load allocations are equal to the ratio of the length of each segment over the total length multiplied by the estimates of direct atmospheric loading for Ballona Creek (3.5 g/day for copper, 2.3 g/day for lead, and 11.7 k/day for zinc).

<u>Dry-weather direct air deposition LAs (total recoverable metals)</u>
<table><tr><th></th><th>Copper (g/day)</th><th>Lead (g/day)</th><th>Zinc (g/day)</th></tr><tr><td>Ballona Creek</td><td>2.0</td><td>1.4</td><td>6.8</td></tr><tr><td>Sepulveda Channel</td><td>0.3</td><td>0.2</td><td>0.9</td></tr></table>
Wet Weather

Wet-weather load allocations for copper, lead, selenium and zinc are developed for direct atmospheric deposition. The mass-based load allocations for direct atmospheric deposition are equal to the percent area of surface water (0.6%) multiplied by the total loading capacity.</td></tr>
</table>

Element	Key Findings and Regulatory Provisions

Wet-weather direct air deposition LAs (total recoverable metals)

	Load Allocation (grams/day)
Copper	1.05E-07 x Daily storm volume (L)
Lead	3.54E-07 x Daily storm volume (L)
Selenium	3.00E-08 x Daily storm volume (L)
Zinc	7.14E-07 x Daily storm volume (L)

Waste Load Allocations *(for point sources)*

Waste load allocations (WLA) are assigned to point sources for Ballona Creek and Sepulveda Canyon Channel. A grouped mass-based waste load allocation is developed for the storm water permittees (Los Angeles County MS4, Caltrans, General Construction and General Industrial) by subtracting the load allocation from the total loading capacity. Concentration-based waste load allocations are developed for other point sources in the watershed.

Dry Weather

Dry-weather waste load allocation for storm water is equal to the dry-weather critical flow multiplied by the dry-weather numeric target minus the load allocation for direct atmospheric deposition.

Dry-weather Storm Water WLAs (grams total recoverable metals/day)

	Copper	Lead	Selenium	Zinc
Ballona Creek	818.9	438.6	171	10,416.2
Sepulveda Channel	370.7	198.8	77	4,711.1

A waste load allocation of zero is assigned to all general construction and industrial storm water permits during dry weather. Therefore, the storm water waste load allocations are apportioned between the MS4 permittees and Caltrans, based on an areal weighting approach.

Dry-weather Storm Water WLAs Apportioned between Storm Water Permits (grams total recoverable metals/day)

	Copper	Lead	Selenium	Zinc
Ballona Creek				
MS4 permittees	807.7	432.6	169	10,273.1
Caltrans	11.2	6.0	2	143.1
Sepulveda Channel				
MS4 Permittees	365.6	196.1	76	4646.4
Caltrans	5.1	2.7	1	64.7

Concentration-based dry-weather waste load allocations are assigned to the minor NPDES permits and general non-storm water NPDES permits that discharge to Ballona Creek or its tributaries. Any future minor NPDES permits or enrollees under a general non-storm water NPDES permit will also be subject to the concentration-based waste load allocations.

Dry-weather WLAs for other permits (total recoverable metals)

Copper (µg/L)	Lead (µg/L)	Selenium (µg/L)	Zinc (µg/L)
24	13	5	304

Element	Key Findings and Regulatory Provisions

Wet Weather

Wet-weather waste load allocation for storm water is equal to the total loading capacity minus the load allocation for direct atmospheric deposition. Wet-weather waste load allocations for the grouped storm water permittees apply to all reaches and tributaries.

Wet-weather Storm Water WLAs (total recoverable metals)

	Waste Load Allocation (grams/day)
Copper	1.79E-05 x Daily storm volume (L)
Lead	5.87E-05 x Daily storm volume (L)
Selenium	4.97E-06 x Daily storm volume (L)
Zinc	1.18E-04 x Daily storm volume (L)

The storm water waste load allocations are apportioned between the MS4 permittees, Caltrans, the general construction and the general industrial storm water permits based on an areal weighting approach.

Wet-weather Storm Water WLAs Apportioned Between Storm Water Permits (total recoverable metals)

	Waste Load Allocation (grams/day)
Copper	
MS4 Permittees	1.70E-05 x Daily storm volume (L)
Caltrans	2.37E-07 x Daily storm volume (L)
General Construction	4.94E-07 x Daily storm volume (L)
General Industrial	1.24E-07 x Daily storm volume (L)
Lead	
MS4 Permittees	5.58E-05 x Daily storm volume (L)
Caltrans	7.78E-07 x Daily storm volume (L)
General Construction	1.62E-06 x Daily storm volume (L)
General Industrial	4.06E-07 x Daily storm volume (L)
Selenium	
MS4 Permittees	4.73E-06 x Daily storm volume (L)
Caltrans	6.59E-08 x Daily storm volume (L)
General Construction	1.37E-07 x Daily storm volume (L)
General Industrial	3.44E-08 x Daily storm volume (L)
Zinc	
MS4 Permittees	1.13E-04 x Daily storm volume (L)
Caltrans	1.57E-06 x Daily storm volume (L)
General Construction	3.27E-06 x Daily storm volume (L)
General Industrial	8.19E-07 x Daily storm volume (L)

Each storm water permittee enrolled under the general construction or industrial storm water permits will receive an individual waste load allocation on a per acre basis, based on the acreage of their facility.

<table>
<tr><th>Element</th><th>Key Findings and Regulatory Provisions</th></tr>
<tr><td></td><td>
<u>Individual per Acre WLAs for General Construction or Industrial Storm Water Permittees (total recoverable metals)</u>
<table>
<tr><td></td><td><u>Waste Load Allocation (grams/day/acre)</u></td></tr>
<tr><td>Copper</td><td>2.20E-10 x Daily storm volume (L)</td></tr>
<tr><td>Lead</td><td>7.20E-10 x Daily storm volume (L)</td></tr>
<tr><td>Selenium</td><td>6.10E-11 x Daily storm volume (L)</td></tr>
<tr><td>Zinc</td><td>1.45E-09 x Daily storm volume (L)</td></tr>
</table>

Concentration-based wet-weather waste load allocations are assigned to the minor NPDES permits and general non-storm water NPDES permits that discharge to Ballona Creek or its tributaries. Any future minor NPDES permits or enrollees under a general non-storm water NPDES permit will also be subject to the concentration-based waste load allocations.
<u>Wet-weather WLAs for other permits (total recoverable metals)</u>
<table>
<tr><th><u>Copper (µg/L)</u></th><th><u>Lead (µg/L)</u></th><th><u>Selenium (µg/L)</u></th><th><u>Zinc (µg/L)</u></th></tr>
<tr><td>18</td><td>59</td><td>5</td><td>119</td></tr>
</table>
</td></tr>
<tr><td>Margin of Safety</td><td>There is an implicit margin of safety through the use of conservative values for the conversion from total recoverable metals to the dissolved fraction during dry and wet weather. In addition, the TMDL includes a margin of safety by evaluating dry-weather and wet-weather conditions separately and assigning allocations based on two disparate critical conditions.</td></tr>
<tr><td>Implementation</td><td>The regulatory mechanisms used to implement the TMDL will include the Los Angeles County Municipal Storm Water NPDES Permit (MS4), the State of California Department of Transportation (Caltrans) Storm Water Permit, minor NPDES permits, general NPDES permits, general industrial storm water NPDES permits, and general construction storm water NPDES permits. Nonpoint sources will be regulated through the authority contained in Sections 13263 and 13269 of the Water Code, in conformance with the State Water Resources Control Board's Nonpoint Source Implementation and Enforcement Policy (May 2004). Each NPDES permit assigned a WLA shall be reopened or amended at re-issuance, in accordance with applicable laws, to incorporate the applicable WLAs as a permit requirement.

The Regional Board shall reconsider this TMDL in five years after the effective date of the TMDL based on additional data obtained from special studies. Table 7-12.2 presents the implementation schedule for the responsible permittees.

Minor NPDES Permits and General Non-Storm Water NPDES Permits:

Permit writers may translate applicable waste load allocations into effluent limits for the minor and general NPDES permits by applying the effluent limitation procedures in Section 1.4 of the State Water Resources Control Board's Policy for Implementation of Toxics Standards for Inland Surface Waters, Enclosed Bays, and Estuaries of</td></tr>
</table>

Element	Key Findings and Regulatory Provisions
	California (2000) or other applicable engineering practices authorized under federal regulations. Compliance schedules may be established in individual NPDES permits, allowing up to 5 years within a permit cycle to achieve compliance. Compliance schedules may not be established in general NPDES permits. A discharger that can not comply immediately with effluent limitations specified to meet waste load allocations will be required to apply for an individual permit, in order to, demonstrate the need for a compliance schedule. Permittees that hold individual NPDES permits and solely discharge storm water may be allowed (at Regional Board discretion) compliance schedules up to 10 years from the effective date of the TMDL to achieve compliance with final WLAs. **General Industrial Storm Water Permits:** The Regional Board will develop a watershed specific general industrial storm water permit to incorporate waste load allocations. Dry-weather Implementation Non-storm water flows authorized by Order No. 97-03 DWQ, or any successor order, are exempt from the dry-weather waste load allocation equal to zero. Instead, these authorized non-storm water flows shall meet the concentration-based waste load allocations assigned to the other NPDES Permits. The dry-weather waste load allocation equal to zero applies to unauthorized non-storm water flows, which are prohibited by Order No. 97-03 DWQ. It is anticipated that the dry-weather waste load allocations will be implemented by requiring improved best management practices (BMPs) to eliminate the discharge of non-storm water flows. However, the permit writers must provide adequate justification and documentation to demonstrate that specified BMPs are expected to result in attainment of the numeric waste load allocations. Wet-weather Implementation The general industrial storm water permittees are allowed interim wet-weather concentration-based waste load allocations based on benchmarks contained in EPA's Storm Water Multi-sector General Permit for Industrial Activities. The interim waste load allocations apply to all industry sectors for a period not to exceed ten years from the effective date of the TMDL. **Interim Wet-Weather WLAs for General Industrial Storm Water Permittees (total recoverable metals)** Copper (µg/L) Lead (µg/L) Selenium (µg/L) Zinc (µg/L) 63.6 81.6 238.5 117 In the first five years from the effective date of the TMDL, interim waste load allocations will not be interpreted as enforceable permit conditions. If monitoring demonstrates that interim waste load

Element	Key Findings and Regulatory Provisions
	allocations are being exceeded, the permittee shall evaluate existing and potential BMPs, including structural BMPs, and implement any necessary BMP improvements. It is anticipated that monitoring results and any necessary BMP improvements would occur as part of an annual reporting process. After five years from the effective date of the TMDL, interim waste load allocations shall be translated into enforceable permit conditions. Compliance with permit conditions may be demonstrated through the installation, maintenance, and monitoring of Regional Board-approved BMPs. If this method of compliance is chosen, permit writers must provide adequate justification and documentation to demonstrate that BMPs are expected to result in attainment of interim waste load allocations. The general industrial storm water permits shall achieve final wet-weather waste load allocations no later than 10 years from the effective date of the TMDL, which shall be expressed as NPDES water quality-based effluent limitations. Effluent limitations may be expressed as permit conditions, such as the installation, maintenance, and monitoring of Regional Board-approved BMPs if adequate justification and documentation demonstrate that BMPs are expected to result in attainment of waste load allocations. **General Construction Storm Water Permits:** Waste load allocations will be incorporated into the State Board general permit upon renewal or into a watershed-specific general permit developed by the Regional Board. <u>Dry-weather Implementation</u> Non-storm water flows authorized by the General Permit for Storm Water Discharges Associated with Construction Activity (Water Quality Order No. 99-08 DWQ), or any successor order, are exempt from the dry-weather waste load allocation equal to zero as long as they comply with the provisions of sections C.3 and A.9 of the Order No. 99-08 DWQ, which state that these authorized non-storm discharges shall be (1) infeasible to eliminate (2) comply with BMPs as described in the Storm Water Pollution Prevention Plan prepared by the permittee, and (3) not cause or contribute to a violation of water quality standards, or comparable provisions in any successor order. Unauthorized non-storm water flows are already prohibited by Order No. 99-08 DWQ. <u>Wet-weather Implementation</u> Within seven years of the effective date of the TMDL, the construction industry will submit the results of BMP effectiveness studies to determine BMPs that will achieve compliance with the final waste load allocations assigned to construction storm water permittees. Regional Board staff will bring the recommended BMPs before the Regional Board for consideration within eight years of the effective date of the TMDL. General construction storm water permittees will be considered

APPENDIX J

Regional Board Resolution No R05-008 for Ballona Creek Estuary Toxics TMDL

Attachment A to Resolution No. R05-008

Amendment to the Water Quality Control Plan – Los Angeles Region to incorporate the Ballona Creek Estuary Toxic Pollutants TMDL

Adopted by the California Regional Water Quality Control Board, Los Angeles Region on July 7, 2005.

Amendments:

Table of Contents
Add:

Chapter 7. Total Maximum Daily Loads (TMDLs) Summaries
7-14 Ballona Creek Estuary Toxic Pollutants TMDL

List of Tables, Figures and Inserts
Add:

Chapter 7. Total Maximum Daily Loads (TMDLs)
Tables
7-14 Ballona Creek Estuary Toxic Pollutants TMDL
7-14.1 Ballona Creek Estuary Toxic Pollutants TMDL: Elements
7-14.2 Ballona Creek Estuary Toxic Pollutants TMDL: Implementation Schedule

Chapter 7. Total Maximum Daily Loads (TMDLs) Summaries, Section 7-14 (Ballona Creek Estuary Toxic Pollutants TMDL)

This TMDL was adopted by the Regional Water Quality Control Board on July 7, 2005.

This TMDL was approved by:

The State Water Resources Control Board on [Insert Date].
The Office of Administrative Law on [Insert Date].
The U.S. Environmental Protection Agency on [Insert Date].

The following tables include the elements of this TMDL.

Table 7-14.1. Ballona Creek Estuary Toxic Pollutants TMDL: Elements

Element	Key Findings and Regulatory Provisions
Problem Statement	Ballona Creek and Ballona Creek Estuary (Estuary) is on the Clean Water Act Section 303(d) list of impaired waterbodies for cadmium, copper, lead, silver, zinc, chlordane, DDT, PCBs and PAHs in sediments. The following designated beneficial uses are impaired by these toxic pollutants: water contact recreation (REC1); non-contact water recreation (REC2); estuarine habitat (EST); marine habitat (MAR); wildlife habitat (WILD); rare and threatened or endangered species (RARE); migration of aquatic organisms (MIGR); reproduction and early development of fish (SPWN); commercial and sport fishing (COMM); and shellfish harvesting (SHELL).
Numeric Target *(Interpretation of the narrative and numeric water quality objective, used to calculate the allocations)*	Numeric water quality targets are based on the sediment quality guidelines compiled by the National Oceanic and Atmospheric Administration, which are used in evaluating waterbodies within the Los Angeles Region for development of the 303(d) list. The Effects Range-Low (ERLs) guidelines are established as the numeric targets for sediments in Ballona Creek Estuary. **Metal Numeric Targets (mg/kg)** Cadmium: 1.2 | Copper: 34 | Lead: 46.7 | Silver: 1.0 | Zinc: 150 **Organic Numeric Targets (ng/kg)** Chlordane: 0.5 | DDTs: 1.58 | Total PCBs: 22.7 | Total PAHs: 4,022
Source Analysis	Urban storm water has been recognized as a substantial source of metals. Numerous researchers have documented that the most prevalent metals in urban storm water (i.e., copper, lead, zinc, and to a lesser degree cadmium) are consistently associated with suspended solids. Because metals are typically associated with fine particles in storm water runoff, they have the potential to accumulate in estuarine sediments where they may pose a risk of toxicity. McPherson et al.[1] estimated that 83% of the cadmium and 86% of the lead were associated with the particle phase in Ballona Creek. Similar to metals, the majority of organic constituents in storm water are associated with particulates, measured concentrations of PAHs, phthalates, and organochlorine compounds in Sepulveda Channel, Centinela Creek, and Ballona Creek found that the majority of these compounds occurred in association with suspended solids. There is toxicity associated with suspended solids in urban runoff discharged from Ballona Creek, as well as with the receiving water sediments. This toxicity is likely attributed to metals and PAHs associated with the suspended sediments.

[1] McPherson, T.N., S.J. Burian, H.J. Turin, M.K. Stenstrom and I.H. Suffet. 2002. Comparison of Pollutant Loads in Dry and Wet Weather Runoff in a Southern California Urban Watershed. *Water Science and Technology* 45:255-261.

<table>
<tr><th>Element</th><th>Key Findings and Regulatory Provisions</th></tr>
<tr><td></td><td>Nonpoint sources are not considered a significant source of toxic pollutants in this TMDL. Nonpoint sources are urban runoff from the Ballona Wetland, since this area discharges directly to the Estuary through a tide gate, and direct atmospheric deposition. The Ballona Wetlands cover approximately 460 acres or 0.6% of the watershed, therefore, loading from this source is considered insignificant. Direct atmospheric deposition of metals and PAHs is considered insignificant because the portion of the Ballona Creek watershed covered by water is small, approximately 480 acres or 0.6% of the watershed. Indirect atmospheric deposition reflects the process by which metals deposited on the land surface may be washed off during storm events and delivered to Ballona Creek and its tributaries. The loading of metals associated with indirect atmospheric deposition are accounted for in the storm water runoff.</td></tr>
<tr><td>Loading Capacity</td><td>TMDLs are developed for cadmium, copper, lead, silver, zinc, chlordane, DDT, PCBs and PAHs within the sediments of the Ballona Creek Estuary.

The loading capacity for Ballona Creek Estuary is calculated by multiplying the numeric targets by the average annual deposition of fine sediment, defined as silts (grain size 0.0625 millimeters) and smaller, within the Estuary by the bulk density of the sediment. The average annual fine sediment deposited is 5,004 cubic meters per year (m^3/yr) and the bulk density is 1.42 metric tons per cubic meter (mt/m^3). The TMDL is set equal to the loading capacity.

Metals Loading Capacity (kilograms/year)
<table>
<tr><th>Cadmium</th><th>Copper</th><th>Lead</th><th>Silver</th><th>Zinc</th></tr>
<tr><td>8.5</td><td>241.6</td><td>332</td><td>7.1</td><td>1,066</td></tr>
</table>
Organics Loading Capacity (grams/year)
<table>
<tr><th>Chlordane</th><th>DDTs</th><th>Total PCBs</th><th>Total PAHs</th></tr>
<tr><td>3.55</td><td>11.2</td><td>161</td><td>28,580</td></tr>
</table></td></tr>
<tr><td>Load Allocations (for nonpoint sources)</td><td>Load allocations (LA) are assigned to nonpoint sources for Ballona Creek Estuary. Load allocations are developed for open space and direct atmospheric deposition.

The mass-based load allocation for open space is equal to the percentage of the watershed covered by the Ballona Wetlands (0.6%) multiplied by the total loading capacity.

Metals Load Allocations for Open Space (kg/yr)
<table>
<tr><th>Cadmium</th><th>Copper</th><th>Lead</th><th>Silver</th><th>Zinc</th></tr>
<tr><td>0.05</td><td>1.4</td><td>2</td><td>0.04</td><td>6</td></tr>
</table>
Organics Load Allocations for Open Space (g/yr)
<table>
<tr><th>Chlordane</th><th>DDTs</th><th>Total PCBs</th><th>Total PAHs</th></tr>
<tr><td>0.02</td><td>0.1</td><td>1</td><td>160</td></tr>
</table></td></tr>
</table>

Element	Key Findings and Regulatory Provisions
	The mass-based load allocation for direct atmospheric deposition is equal to the percentage of the watershed covered by water (0.6%) multiplied by the total loading capacity. **Metals Load Allocations for Direct Atmospheric Deposition (kg/yr)** Cadmium: 0.05 | Copper: 1.4 | Lead: 2 | Silver: 0.04 | Zinc: 6 **Organics Load Allocations for Direct Atmospheric Deposition (g/yr)** Chlordane: 0.02 | DDTs: 0.1 | Total PCBs: 1 | Total PAHs: 170
Waste Load Allocations *(for point sources)*	Waste load allocations (WLA) are assigned to point sources for the Ballona Creek watershed. A grouped mass-based waste load allocation is developed for the storm water permittees (Los Angeles County MS4, Caltrans, General Construction and General Industrial) by subtracting the load allocations from the total loading capacity. Concentration-based waste load allocations are developed for other point sources in the watershed. **Metals Waste Load Allocations for Storm Water (kg/yr)** Cadmium: 8.4 | Copper: 238.8 | Lead: 328 | Silver: 7.02 | Zinc: 1,054 **Organics Waste Load Allocations for Storm Water (g/yr)** Chlordane: 3.51 | DDTs: 11 | Total PCBs: 159 | Total PAHs: 28,250 The storm water waste load allocations are apportioned between the MS4 permittees, Caltrans, the general construction and the general industrial storm water permits based on an areal weighting approach. **Metals Storm Water WLAs Apportioned between Permits (kg/yr)** MS4 Permittees: Cadmium 8.0, Copper 227.3, Lead 312.3, Silver 6.69, Zinc 1003 Caltrans: Cadmium 0.11, Copper 3.2, Lead 4.4, Silver 0.09, Zinc 14 General Construction: Cadmium 0.23, Copper 6.6, Lead 9.1, Silver 0.20, Zinc 29 General Industrial: Cadmium 0.06, Copper 1.7, Lead 2.3, Silver 0.05, Zinc 7 **Organics Storm Water WLAs Apportioned between Permits (g/yr)** MS4 Permittees: Chlordane 3.34, DDTs 10.56, Total PCBs 152, Total PAHs 26,900 Caltrans: Chlordane 0.05, DDTs 0.15, Total PCBs 2, Total PAHs 400 General Construction: Chlordane 0.10, DDTs 0.31, Total PCBs 4, Total PAHs 800 General Industrial: Chlordane 0.02, DDTs 0.08, Total PCBs 1, Total PAHs 200 Each storm water permittee enrolled under the general construction or industrial storm water permits will receive an individual waste load allocation on a per acre basis, based on the acreage of their facility.

<table>
<tr><th>Element</th><th>Key Findings and Regulatory Provisions</th></tr>
<tr><td></td><td>
Metals per Acre WLAs for Individual General Construction or Industrial Storm Water Permittees (g/yr/ac)
<table>
<tr><th>Cadmium</th><th>Copper</th><th>Lead</th><th>Silver</th><th>Zinc</th></tr>
<tr><td>0.1</td><td>3</td><td>4</td><td>0.1</td><td>13</td></tr>
</table>
Organics per Acre WLAs for Individual General Construction or Industrial Storm Water Permittees (mg/yr/ac)
<table>
<tr><th>Chlordane</th><th>DDTs</th><th>Total PCBs</th><th>Total PAHs</th></tr>
<tr><td>0.04</td><td>0.14</td><td>2</td><td>350</td></tr>
</table>
Concentration-based waste load allocations are assigned to the minor NPDES permits and general non-storm water NPDES permits that discharge to Ballona Creek or its tributaries. Any future minor NPDES permits or enrollees under a general non-storm water NPDES permit will also be subject to the concentration-based waste load allocations.
Metals Concentration-based Waste Load Allocations (mg/kg)
<table>
<tr><th>Cadmium</th><th>Copper</th><th>Lead</th><th>Silver</th><th>Zinc</th></tr>
<tr><td>1.2</td><td>34</td><td>46.7</td><td>1.0</td><td>150</td></tr>
</table>
Organic Concentration-based Waste Load Allocations (ug/kg)
<table>
<tr><th>Chlordane</th><th>DDTs</th><th>Total PCBs</th><th>Total PAHs</th></tr>
<tr><td>0.5</td><td>1.58</td><td>22.7</td><td>4,022</td></tr>
</table>
</td></tr>
<tr><td>Margin of Safety</td><td>An implicit margin of safety is applied through the use of the more protective sediment quality guideline values. The ERLs were selected over the higher ERMs as the numeric targets.</td></tr>
<tr><td>Implementation</td><td>The regulatory mechanisms used to implement the TMDL will include the Los Angeles County Municipal Storm Water NPDES Permit (MS4), the State of California Department of Transportation (Caltrans) Storm Water Permit, minor NPDES permits, general NPDES permits, general industrial storm water NPDES permits, general construction storm water NPDES permits. Nonpoint sources will be regulated through the authority contained in sections 13263 and 13269 of the Water Code, in conformance with the State Water Resources Control Board's Nonpoint Source Implementation and Enforcement Policy (May 2004). Each NPDES permit assigned a WLA shall be reopened or amended at re-issuance, in accordance with applicable laws, to incorporate the applicable WLAs as a permit requirement.

The Regional Board shall reconsider this TMDL in six years after the effective date of the TMDL based on additional data obtained from special studies. Table 7-14.2 presents the implementation schedule for the responsible permittees.</td></tr>
</table>

Element	Key Findings and Regulatory Provisions
	Minor NPDES Permits and General Non-Storm Water NPDES Permits: The concentration-based waste load allocations for the minor NPDES permits and general non-storm water NPDES permits will be implemented through NPDES permit limits. Permit writers may translate applicable waste load allocations into effluent limits for the minor and general NPDES permits by applying applicable engineering practices authorized under federal regulations. The minor and general non-storm water NPDES permittees are allowed up to seven years from the effective date of the TMDL to achieve the waste load allocations. **General Industrial Storm Water Permit:** The Regional Board will develop a watershed specific general industrial storm water permit to incorporate waste load allocations. Concentration-based permit limits may be set to achieve the mass-based waste load allocations. These concentration-based limits would be equal to the concentration-based waste load allocations assigned to the other NPDES permits. It is expected that permit writers will translate the waste load allocations into BMPs, based on BMP performance data. However, the permit writers must provide adequate justification and documentation to demonstrate that specified BMPs are expected to result in attainment of the numeric waste load allocations. The general industrial storm water permittees are allowed up to seven years from the effective date of the TMDL to achieve the waste load allocations. **General Construction Storm Water Permit:** Waste load allocations will be incorporated into the State Board general permit upon renewal or into a watershed specific general construction storm water permit developed by the Regional Board. Within seven years of the effective date of the TMDL, the construction industry will submit the results of BMP effectiveness studies to determine BMPs that will achieve compliance with the waste load allocations assigned to construction storm water permittees. Regional Board staff will bring the recommended BMPs before the Regional Board for consideration within eight years of the effective date of the TMDL. General construction storm water permittees will be considered in compliance with waste load allocations if they implement these Regional Board approved BMPs. All general construction permittees must implement the approved BMPs within nine years of the effective date of the TMDL. If no effectiveness studies are conducted and no BMPs are approved by the Regional Board within eight years of the effective date of the TMDL, each general construction storm water permit holder will be subject to site-specific BMPs and monitoring requirements to demonstrate compliance with waste load allocations.

Element	Key Findings and Regulatory Provisions
	MS4 and Caltrans Storm Water Permits: The County of Los Angeles, City of Los Angeles, Beverly Hills, Culver City, Inglewood, Santa Monica, and West Hollywood are jointly responsible for meeting the mass-based waste load allocations for the MS4 permittees. Caltrans is responsible for meeting their mass-based waste load allocations, however, they may choose to work with the MS4 permittees. The primary jurisdiction for the Ballona Creek watershed is the City of Los Angeles. Each municipality and permittee will be required to meet the waste load allocations at the designated TMDL effectiveness monitoring points. A phased implementation approach, using a combination of non-structural and structural BMPs may be used to achieve compliance with the waste load allocations. The administrative record and the fact sheets for the MS4 and Caltrans storm water permits must provide reasonable assurance that the BMPs selected will be sufficient to implement the numeric waste load allocations. We expect that reductions to be achieved by each BMP will be documented and that sufficient monitoring will be put in place to verify that the desired reductions are achieved. The permits should also provide a mechanism to adjust the required BMPs as necessary to ensure their adequate performance. The implementation schedule for the MS4 and Caltrans permittees consists of a phased approach, with compliance to be achieved in prescribed percentages of the watershed, with total compliance to be achieved within 15 years.
Seasonal Variations and Critical Conditions	There is a high degree of inter- and intra-annual variability in sediments deposited at the mouth of Ballona Creek. This is a function of the storms, which are highly variable between years. Studies by the Army Corps of Engineers have shown that sediment delivery to Ballona Creek is related to the size of the storm (USACE, 2003). The TMDL is based on a long-term average deposition patterns over a 10-year period from 1991 to 2001. This time period contains a wide range of storm conditions and flows in the Ballona Creek watershed. Use of the average condition for the TMDL is appropriate because issues of sediment effects on benthic communities and potential for bioaccumulation to higher trophic levels occurs over long time periods.
Monitoring	Effective monitoring will be required to assess the condition of Ballona Creek and Estuary and to assess the on-going effectiveness of efforts by dischargers to reduce toxic pollutants loading to the Ballona Creek Estuary. Special studies may also be appropriate to provide further information about new data, new or alternative sources, and revised scientific assumptions. Below the Regional Board identifies the various goals of monitoring efforts and studies. The programs, reports, and studies will be developed in response to subsequent orders issued by the Executive Officer.

Element	Key Findings and Regulatory Provisions
	Ambient Monitoring An ambient monitoring program is necessary to assess water quality throughout Ballona Creek and its tributaries and to assess the progress being made to remove the toxic pollutant impairments in Ballona Creek Estuary sediments. Data on background water quality for organics and sediments will help refine the numeric targets and waste load allocations and assist in the effective placement of BMPs. In addition, fish and mussel tissue data is required in Ballona Creek Estuary to confirm the fish tissue listings. Water quality samples shall be collected from Ballona Creek and Estuary monthly and analyzed for cadmium, copper, lead, silver, zinc, chlordane, dieldrin, DDT, total PCBs and total PAHs at detection limits that are at or below the minimum levels until the TMDL is reconsidered in the sixth year. The minimum levels are those published by the State Water Resources Control Board in Appendix 4 of the Policy for the Implementation of Toxic Standards for Inland Surface Water, Enclosed Bays, and Estuaries of California, March 2, 2000. Special emphasis should be placed on achieving detection limits that will allow evaluation relative to the CTR standards. If these can not be achieved with conventional techniques, then a special study should be proposed to evaluate concentrations of organics. Storm water monitoring conducted as part of the MS4 storm water monitoring program should continue to provide assessment of water quality during wet-weather conditions and loading estimates from the watershed to the Estuary. If analysis of chlordane, dieldrin, DDT, total PCBs or total PAHs are not currently part of the sampling programs these organics should be added. In addition, special emphasis should be placed on achieving lower detection limits for DDTs, PCBs and PAHs. The MS4 and Caltrans storm water permittees are jointly responsible for conducting bioaccumulation testing of fish and mussel tissue within the Estuary. The permittees are required to submit for approval of the Executive Officer a monitoring plan that will provide the data needed to confirm the 303(d) listing or delisting, as applicable. Representative sediment sampling locations shall be randomly selected within the Estuary and analyzed for cadmium, copper, lead, silver, zinc, chlordane, dieldrin, DDT, total PCBs and total PAHs at detection limits that are lower than the ERLs. Sediment samples shall also be analyzed for total organic carbon, grain size and sediment toxicity testing. Initial sediment monitoring should be done quarterly in the first year of the TMDL to define the baseline and semi-annually, thereafter, to evaluate effectiveness of the BMPs until the TMDL is reconsidered in the sixth year. The sediment toxicity testing shall include testing of multiple species, a minimum of three, for lethal and non-lethal endpoints. Toxicity testing may include: the 28-day and 10-day amphipod mortality test; the sea

Element	Key Findings and Regulatory Provisions
	urchin fertilization testing of sediment pore water; and the bivalve embryo testing of the sediment/water interface. The chronic 28-day and shorter-term 10-day amphipod tests may be conducted in the initial year of quarterly testing and the results compared. If there is no significant difference in the tests, then the less expensive 10-day test can be used throughout the rest of the monitoring, with some periodic 28-day testing. **TMDL Effectiveness Monitoring** The water quality samples collected during wet weather as part of the MS4 storm water monitoring program shall be analyzed for total dissolved solids, settable solids and total suspended solids if not already part of the existing sampling program. Sampling shall be designed to collect sufficient volumes of settable and suspended solids to allow for analysis of cadmium, copper, lead, silver, zinc, chlordane, dieldrin, total DDT, total PCBs, total PAHs, and total organic carbon in the bulk sediment. Semi-annually, representative sediment sampling locations shall be randomly selected within the Estuary and analyzed for cadmium, copper, lead, silver, zinc, chlordane, dieldrin, DDT, total PCBs, and total PAHs at detection limits that are lower than the ERLs. The sediment samples shall also be analyzed for total organic carbon, grain size and sediment toxicity. The sediment toxicity testing shall include testing of multiple species, a minimum of three, for lethal and non-lethal endpoints. Toxicity testing may include: the 28-day and 10-day amphipod mortality test; the sea urchin fertilization testing of sediment pore water; and the bivalve embryo testing of the sediment/water interface. Toxicity shall be indicated by an amphipod survival rate of 70% or less in a single test. Accelerated monitoring shall be conducted to confirm toxicity at stations identified as toxic. Accelerated monitoring shall consist of six additional tests, approximately every two weeks, over a 12-week period. If the results of any two of the six accelerated tests are less than 90% survival, then the MS4 and Caltrans permittees shall conduct a Toxicity Identification Evaluation (TIE). The TIE shall include reasonable steps to identify the sources of toxicity and steps to reduce the toxicity. The Phase I TIE shall include the following treatments and corresponding blanks: baseline toxicity; particle removal by centrifugation; solid phase extraction of the centrifuged sample using C8, C18, or another media; complexation of metals using ethylenediaminetetraacetic acid (EDTA) addition to the raw sample; neutralization of oxidants/metals using sodium thiosulfate addition to the raw sample; and inhibition of organo-phosphate (OP) pesticide activation using piperonyl butoxide addition to the raw sample (crustacean toxicity tests only).

Element	Key Findings and Regulatory Provisions
	Bioaccumulation monitoring of fish and mussel tissue within the Estuary shall be conducted. The permittees are required to submit for approval of the Executive Officer a monitoring plan that will provide the data needed to assess the effectiveness of the TMDL. The general industrial storm water permit shall contain a model monitoring and reporting program to evaluate BMP effectiveness. A permittee enrolled under the general industrial permit shall have the choice of conducting individual monitoring based on the model program or participating in a group monitoring effort. MS4 permittees are encouraged to take the lead in group monitoring efforts for industrial facilities within their jurisdiction because compliance with waste load allocations by these facilities will in many cases translate to reductions in contaminate loads to the MS4 system. **Special Studies** Special studies are recommended to refine source assessments, to provide better estimates of loading capacity, and to optimize implementation efforts. The Regional Board will re-consider the TMDL in the sixth year after the effective date in light of the findings of these studies. Special studies may include: • Evaluation and use of low detection level techniques to evaluate water quality concentrations for those contaminants where standard detection limits cannot be used to assess compliance for CTR standards or are not sufficient for estimating source loadings from tributaries and storm water. • Developing and implementing a monitoring program to collection the data necessary to apply a multiple lines of evidence approach. • Evaluation and use of sediment TIEs to evaluate causes of any recurring sediment toxicity. • Evaluate partitioning coefficients between water column and sediment to assess the contribution of water column discharges to sediment concentrations in the Estuary. • Studies to refine relationship between pollutants and suspended solids aimed at better understanding of the delivery of pollutants to the watershed. • Studies to understand transport of sediments to the estuary, including the relationship between storm flows, sediment loadings to the estuary, and sediment deposition patterns within the estuary. • Studies to evaluate effectiveness of BMPs to address pollutants and/or sediments.

Table 7-14.2. Ballona Creek Estuary Toxic Pollutants TMDL: Implementation Schedule

Date	Action
Effective date of the TMDL	Regional Board permit writers shall incorporate the waste load allocations for sediment into the NPDES permits. Waste load allocations will be implemented through NPDES permit limits in accordance with the implementation schedule contained herein, at the time of permit issuance, renewal or re-opener.
Within 6 months after the effective date of the State Board adopted sediment quality objectives and implementation policy	The Regional Board will re-assess the numeric targets and waste load allocations for consistency with the State Board adopted sediment quality objectives.
5 years after effective date of the TMDL	Responsible jurisdictions and agencies shall provide to the Regional Board result of any special studies.
6 years after effective date of the TMDL	The Regional Board shall reconsider this TMDL to re-evaluate the waste load allocations and the implementation schedule.
MINOR NPDES PERMITS AND GENERAL NON-STORM WATER NPDES PERMITS	
7 years after effective date of the TMDL	The non-storm water NPDES permits shall achieve the concentration-based waste load allocations for sediment per provisions allowed for in NPDES permits.
GENERAL INDUSTRIAL STORM WATER PERMIT	
7 years after effective date of the TMDL	The general industrial storm water permits shall achieve the mass-based waste load allocations for sediment per provisions allowed for in NPDES permits. Permits shall allow an iterative BMP process including BMP effectiveness monitoring to achieve compliance with permit requirements.
GENERAL CONSTRUCTION STORM WATER PERMIT	
7 years from the effective date of the TMDL	The construction industry will submit the results of the BMP effectiveness studies to the Regional Board for consideration. In the event that no effectiveness studies are conducted and no BMPs are approved, permittees shall be subject to site-specific BMPs and monitoring to demonstrate BMP effectiveness.
8 years from the effective date of the TMDL	The Regional Board will consider results of the BMP effectiveness studies and consider approval of BMPs no later than six years from the effective date of the TMDL.
9 years from the effective date of the TMDL	All general construction storm water permittees shall implement Regional Board-approved BMPs.

Date	Action
MS4 AND CALTRANS STORM WATER PERMITS	
12 months after the effective date of the TMDL.	In response to an order issued by the Executive Officer, the MS4 and Caltrans storm water NPDES permittees must submit a coordinated monitoring plan, to be approved by the Executive Officer, which includes both ambient monitoring and TMDL effectiveness monitoring. Once the coordinated monitoring plan is approved by the Executive Officer, ambient monitoring shall commence.
5 years after effective date of TMDL (Draft Report) 5 ½ years after effective date of TMDL (Final Report)	The MS4 and Caltrans storm water NPDES permittees shall provide a written report to the Regional Board outlining how they will achieve the waste load allocations for sediment to Ballona Creek Estuary. The report shall include implementation methods, an implementation schedule, proposed milestones, and any applicable revisions to the TMDL effectiveness monitoring plan.
7 years after effective date of the TMDL	The MS4 and Caltrans storm water NPDES permittees shall demonstrate that 25% of the total drainage area served by the MS4 system is effectively meeting the waste load allocations for sediment.
9 years after effective date of the TMDL	The MS4 and Caltrans storm water NPDES permittees shall demonstrate that 50% of the total drainage area served by the MS4 system is effectively meeting the waste load allocations for sediment.
11 years after effective date of the TMDL	The MS4 and Caltrans storm water NPDES permittees shall demonstrate that 75% of the total drainage area served by the MS4 system is effectively meeting the waste load allocations for sediment.
15 years after effective date of the TMDL	The MS4 and Caltrans storm water NPDES permittees shall demonstrate that 100% of the total drainage area served by the MS4 system is effectively meeting the waste load allocations for sediment.

Element	Key Findings and Regulatory Provisions
	in compliance with final waste load allocations if they implement these Regional Board approved BMPs. All permittees must implement the approved BMPs within nine years of the effective date of the TMDL. If no effectiveness studies are conducted and no BMPs are approved by the Regional Board within eight years of the effective date of the TMDL, each general construction storm water permit holder will be subject to site-specific BMPs and monitoring requirements to demonstrate compliance with final waste load allocations. **MS4 and Caltrans Storm Water Permits:** The County of Los Angeles, City of Los Angeles, Beverly Hills, Culver City, Inglewood, Santa Monica, and West Hollywood are jointly responsible for meeting the mass-based waste load allocations for the MS4 permittees. Caltrans is responsible for meeting their mass-based waste load allocations, however, they may choose to work with the MS4 permittees. The primary jurisdiction for the Ballona Creek watershed is the City of Los Angeles. Applicable CTR limits are being met most of the time during dry weather, with episodic exceedances. Due to the expense of obtaining accurate flow measurements required for calculating loads, concentration-based permit limits may apply during dry weather. These concentration-based limits would be equal to the dry-weather concentration-based waste load allocations assigned to the other NPDES permits. Each municipality and permittee will be required to meet the storm water waste load allocation at the designated TMDL effectiveness monitoring points. A phased implementation approach, using a combination of non-structural and structural BMPs may be used to achieve compliance with the stormwater waste load allocations. The administrative record and the fact sheets for the MS4 and Caltrans storm water permits must provide reasonable assurance that the BMPs selected will be sufficient to implement the waste load allocations. The implementation schedule for the MS4 and Caltrans permittees consists of a phased approach, with compliance to be achieved in prescribed percentages of the watershed, with total compliance to be achieved within 15 years.
Seasonal Variations and Critical Conditions	Seasonal variations are addressed by developing separate waste load allocations for dry weather and wet weather. Based on long-term flow records, dry-weather flows in Ballona Creek are estimated to be 14 cubic feet per second (cfs). Since, this flow has been very consistent, 14 cfs is used to define the critical dry-weather flow for Ballona Creek at Sawtelle Boulevard (upstream of Sepulveda Canyon Channel). There are no historic flow records to determine the average long-term flows for Sepulveda Canyon Channel. Therefore, in the absence of historical records the 2003 dry-weather characterization study measurements are assumed reasonable estimates of flow for this

Element	Key Findings and Regulatory Provisions
	channel. The critical dry-weather flow for Sepulveda Canyon Channel is defined as the average flow of 6.3 cfs. Wet-weather allocations are developed using the load-duration curve concept. The total wet-weather waste load allocation varies by storm, therefore, given this variability in storm water flows, no justification was found for selecting a particular sized storm as the critical condition.
Monitoring	Effective monitoring will be required to assess the condition of the Ballona Creek and to assess the on-going effectiveness of efforts by dischargers to reduce metals loading to Ballona Creek. Special studies may also be appropriate to provide further information about new data, new or alternative sources, and revised scientific assumptions. Below the Regional Board identifies the various goals of monitoring efforts and studies. The programs, reports, and studies will be developed in response to subsequent orders issued by the Executive Officer. **Ambient monitoring** An ambient monitoring program is necessary to assess water quality throughout Ballona Creek and its tributaries and the progress being made to remove the metals impairments. The MS4 and Caltrans storm water NPDES permittees are jointly responsible for implementing the ambient monitoring program. The responsible agencies shall analyze samples for total recoverable metals and dissolved metals, including cadmium and silver, and hardness once a month at each monitoring location. The reported detection limits shall be lower than the hardness adjusted CTR criteria to determine if water quality objectives are being met. There are three ambient monitoring locations. **Ambient Monitoring Locations** Waterbody — Location Ballona Creek — At Sawtelle Boulevard Sepulveda Channel — Just Above the Confluence with Ballona Creek Ballona Creek — At Inglewood Boulevard **TMDL Effectiveness Monitoring** The MS4 and Caltrans storm water NPDES permittees are jointly responsible for assessing the progress in reducing pollutant loads to achieve the TMDL. The MS4 and Caltrans storm water NPDES permittees are required to submit for approval of the Executive Officer a coordinated monitoring plan that will demonstrate the effectiveness of the phased implementation schedule for this TMDL, which requires attainment of the applicable waste load allocations in prescribed percentages of the watershed over a 15-year period. The monitoring locations specified for the ambient monitoring program may be used as the effectiveness monitoring locations. The MS4 and Caltrans storm water NPDES permittees will be found to be effectively meeting the dry-weather waste load allocations if the in-stream pollutant concentrations or load at the first downstream monitoring location is equal to or less than the corresponding

Element	Key Findings and Regulatory Provisions
	concentration- or load-based waste load allocation. Alternatively, effectiveness of the TMDL may be assessed at the storm drain outlet based on the concentration-based waste load allocation for the receiving water. For storm drains that discharge to other storm drains, the waste load allocation will be based on the waste load allocation for the ultimate receiving water for that storm drain system. The MS4 and Caltrans storm water NPDES permittees will be found to be effectively meeting the wet-weather waste load allocations if the loading at the most downstream monitoring location is equal to or less then the wet-weather waste load allocation. Compliance with individual general construction and industrial storm water permittees will be based on monitoring of discharges at the property boundary. Compliance may be assessed based on concentration and/or load allocations. The general storm water permits shall contain a model monitoring and reporting program to evaluate BMP effectiveness. A permittee enrolled under the general permits shall have the choice of conducting individual monitoring based on the model program or participating in a group monitoring effort. MS4 permittees are encouraged to take the lead in group monitoring efforts for industrial facilities under their jurisdiction because compliance with waste load allocations by these facilities will in many cases translate to reductions in metals loads to the MS4 system. **Special studies** The implementation schedule, Table 7-12.2, allows time for special studies that may serve to refine the estimate of loading capacity, waste load and/or load allocations, and other studies that may serve to optimize implementation efforts. The Regional Board will re-consider the TMDL in the fifth year after the effective date in light of the findings of these studies. Studies may include: • Refinement of hydrologic and water quality model • Additional source assessment • Refinement of potency factors correlation between total suspended solids and metals loadings during dry and wet weather • Correlation between short-term rainfall intensity and metals loadings for use in sizing in-line structural BMPs • Correlation between storm volume and total recoverable metals loading for use in sizing storm water retention facilities • Refined estimates of metals partitioning coefficients, conversion factors, and site-specific toxicity. • Evaluation of potential contribution of aerial deposition and sources of aerial deposition.

Table 7-12.2. Ballona Creek Metals TMDL: Implementation Schedule

Date	Action
Effective date of the TMDL	Regional Board permit writers shall incorporate the waste load allocations into the NPDES permits. Waste load allocations will be implemented through NPDES permit limits in accordance with the implementation schedule contained herein, at the time of permit issuance or re-issuance.
4 years after effective date of the TMDL	Responsible jurisdictions and agencies shall provide to the Regional Board results of the special studies.
5 years after effective date of the TMDL	The Regional Board shall reconsider this TMDL to re-evaluate the waste load allocations and the implementation schedule.
MINOR NPDES PERMITS AND GENERAL NON-STORM WATER NPDES PERMITS	
Upon permit issuance or renewal	The non-storm water NPDES permittees shall achieve the waste load allocations, which shall be expressed as NPDES water quality-based effluent limitations specified in accordance with federal regulations and state policy on water quality control. Compliance schedules may allow up to five years in individual NPDES permits to meet permit requirements. Compliance schedules may not be established in general NPDES permits. Permittees that hold individual NPDES permits and solely discharge storm water may be allowed (at Regional Board discretion) compliance schedules up to 10 years from the effective date of the TMDL to achieve compliance with final WLAs.
GENERAL INDUSTRIAL STORM WATER PERMITS	
Upon permit issuance or renewal	The general industrial storm water NPDES permittees shall achieve dry-weather waste load allocations, which shall be expressed as NPDES water quality-based effluent limitations specified in accordance with federal regulations and state policy on water quality control. Effluent limitations may be expressed as permit conditions, such as the installation, maintenance, and monitoring of Regional Board-approved BMPs. Permittees shall begin to install and test BMPs to meet the interim wet-weather WLAs. BMP effectiveness monitoring will be implemented to determine progress in achieving interim wet-weather waste load allocations.
5 years after effective date of the TMDL	The general industrial storm water NPDES permittees shall achieve the interim wet-weather waste load allocations, which shall be expressed as NPDES water quality-based effluent limitations specified in accordance with federal regulations and state policy on water quality control. Effluent limitations may be expressed as permit conditions, such as the installation, maintenance, and monitoring of Regional Board-approved BMPs. Permittees shall begin an iterative BMP process including BMP effectiveness monitoring to achieve compliance

Date	Action
	with final wet-weather WLAs.
10 years after the effective date of the TMDL	The general industrial storm water NPDES permittees shall achieve the final wet-weather waste load allocations, which shall be expressed as NPDES water quality-based effluent limitations specified in accordance with federal regulations and state policy on water quality control. Effluent limitations may be expressed as permit conditions, such as the installation, maintenance, and monitoring of Regional Board-approved BMPs.
GENERAL CONSTRUCTION STORM WATER PERMITS	
Upon permit issuance, renewal, or re-opener	Non-storm water flows not authorized by Order No. 99-08 DWQ, or any successor order, shall achieve dry-weather waste load allocations of zero. Waste load allocations shall be expressed as NPDES water quality-based effluent limitations specified in accordance with federal regulations and state policy on water quality control. Effluent limitations may be expressed as permit conditions, such as the installation, maintenance, and monitoring of Regional Board-approved BMPs.
7 years from the effective date of the TMDL	The construction industry will submit the results of wet-weather BMP effectiveness studies to the Regional Board for consideration. In the event that no effectiveness studies are conducted and no BMPs are approved, permittees shall be subject to site-specific BMPs and monitoring to demonstrate BMP effectiveness.
8 years from the effective date of the TMDL	The Regional Board will consider results of the wet-weather BMP effectiveness studies and consider approval of BMPs no later than six years from the effective date of the TMDL.
9 years from the effective date of the TMDL	All general construction storm water permittees shall implement Regional Board-approved BMPs.
MS4 AND CALTRANS STORM WATER PERMITS	
12 months after the effective date of the TMDL	In response to an order issued by the Executive Officer, the MS4 and Caltrans storm water NPDES permittees must submit a coordinated monitoring plan, to be approved by the Executive Officer, which includes both ambient monitoring and TMDL effectiveness monitoring. Once the coordinated monitoring plan is approved by the Executive Officer ambient monitoring shall commence.
48 months after effective date of TMDL (Draft Report) 54 months after effective date of TMDL (Final Report)	MS4 and Caltrans storm water NPDES permittees shall provide a written report to the Regional Board outlining the drainage areas to be address and how these areas will achieve compliance with the waste load allocations. The report shall include implementation methods, an implementation schedule,

Date	Action
	proposed milestones, and any applicable revisions to the TMDL effectiveness monitoring plan.
6 years after effective date of the TMDL	The MS4 and Caltrans storm water NPDES permittees shall demonstrate that 50% of the total drainage area served by the MS4 system is effectively meeting the dry-weather waste load allocations and 25% of the total drainage area served by the MS4 system is effectively meeting the wet-weather waste load allocations.
8 years after effective date of the TMDL	The MS4 and Caltrans storm water NPDES permittees shall demonstrate that 75% of the total drainage area served by the MS4 system is effectively meeting the dry-weather waste load allocations.
10 years after effective date of the TMDL	The MS4 and Caltrans storm water NPDES permittees shall demonstrate that 100% of the total drainage area served by the MS4 system is effectively meeting the dry-weather waste load allocations and 50% of the total drainage area served by the MS4 system is effectively meeting the wet-weather waste load allocations.
15 years after effective date of the TMDL	The MS4 and Caltrans storm water NPDES permittees shall demonstrate that 100% of the total drainage area served by the MS4 system is effectively meeting both the dry-weather and wet-weather waste load allocations.

APPENDIX K

Participating Organizations Contacts (Monitoring)

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APPENDIX L

Basin Plan

The Los Angeles Regional Water Quality Control Board's (Regional Board) Basin Plan is designed to preserve and enhance water quality and protect the beneficial uses of all regional waters. Specifically, the Basin Plan (i) designates beneficial uses for surface and ground waters, (ii) sets narrative and numerical objectives that must be attained or maintained to protect the designated beneficial uses and conform to the state's antidegradation policy, and (iii) describes implementation programs to protect all waters in the Region. In addition, the Basin Plan incorporates (by reference) all applicable State and Regional Board plans and policies and other pertinent water quality policies and regulations. Those of other agencies are referenced in appropriate sections throughout the Basin Plan.

The Basin Plan is a resource for the Regional Board and others who use water and/or discharge wastewater in the Los Angeles Region. Other agencies and organizations involved in environmental permitting and resource management activities also use the Basin Plan. Finally the Basin Plan provides valuable information to the public about local water quality issues.

The Basin Plan is reviewed and updated as necessary. Following adoption by the Regional Board, the Basin Plan and subsequent amendments are subject to approval by the State Board, the State Office of Administrative Law (OAL), and the United States Environmental Protection Agency (USEPA).

The Basin Plan can be downloaded from the Regional Board's website:

http://www.swrcb.ca.gov/rwqcb4/html/meetings/tmdl/Basin_plan/basin_plan.html

APPENDIX M

Safety

Driving Safety & Reporting Vehicle Accidents

During sample collection, 4-wheel drive mode should be used on the sand. It is best to use 4-lo when driving on the sand in 4-wheel drive (4WD). Tire pressure should equal 20-25 psi for the small truck, and 35 psi for the large truck. If there is some problem driving on the sand (i.e., stuck or barely moving) the tire pressure is decreased to 15 psi then when off the sand re-inflated to 20 psi. When the sampler arrives back at the lab, the tire pressure is increased back up to 25 psi. The sampler needs to exit 4WD when leaving the sand for street driving. When driving with tires at minimum activation pressure range (as recommended by the National Highway Traffic Safety Administration), one should not exceed 65 MPH on the freeway and drive for no longer than 60 minutes at high speed. Safety issues related to tires and tire pressure may be found at this website: http://www.nhtsa.dot.gov/cars/rules/rulings/TirePresFinal.

The Life Guard speed limit on the sand is 15 MPH, dependent upon conditions. At no time is driving faster than 15 MPH allowable. Observe the speed limit and anticipate the possibility of people covered in sand or otherwise obscured from view. Be extremely cautious when children are present.

The following are additional precautions for City of L.A.'s EMD and participating laboratories' personnel to use as guidelines while driving a 4WD vehicle to collect samples:

a. Drivers of city vehicles must have a valid operating license.
b. If persons in vehicle observe a potentially unsafe condition with the vehicle, discontinue operation, return the vehicle, and report the problem to management and Fleet Services.
c. Vehicle occupants must wear safety belts and ensure the vehicle contains an accident-reporting envelope.
d. Cargo items should not be stacked above seat level; if they are, a safety screen should be installed.
e. Employee responsibility:
   It is the responsibility of every City employee who drives, is in control of, or is responsible for any City-owned, rented or mileage vehicle which is involved in an accident (no matter how slight) to notify the proper authorities and to fill out the proper forms in case of a vehicle accident.

   Detailed instructions on what to do are contained in the packet (form Gen. 84) which is kept in the glove compartment of every City-owned or mileage vehicle. If the vehicle you are using does not contain a packet, you may obtain one by calling any Fleet Services facility where City vehicles are maintained. Included in the packet is form Gen. 88, which is the automobile accident report. This form has five copies, which are to be distributed to the

locations printed on the top of the form. This written report must be filed with the City Attorney within 24 hours of the accident.
If a vehicle accident occurs, the driver must report the accident to the police by notifying the Police Complaint Board at 213-485-2683 or 213-623-3311. For emergencies, dial 911. Additionally, if any injury or death has occurred, you must report the accident by phone to the City Attorney, Automobile Liability Division, at 213-485-3634. If no one answers, have the City Hall Chief Operator, at 213-485-5500, relay your call. If an EMD employee is injured, contact the Workers' Compensation Division at 213-847-9405 to report the injury. All City/EMD vehicles involved in accidents must be brought to Fleet Services (213-485-4985) for inspection within five working days.

All accidents must be reported including:

- When an accident occurs in a County or incorporated area,
- When a driver is accused of being in an accident but has no knowledge of same,
- When an animal is seriously injured or killed. Search for the owner and report the incident.
- When two City vehicles are involved in an accident,
- When the accident occurs on a freeway.

The Occupational Safety Office must be notified if there is death or serious injury caused by the vehicular accident. The Occupational Safety Office telephone number is 213-485-4691. Call The City Hall Chief Operator at 213-485-5500 and ask for a safety engineer if the accident occurs after working hours.

The driver must remain on the scene of the accident and obtain information from other persons involved. The driver should also have witnesses fill out the witness cards located in the packet of information and forms in the glove compartment.

f. Supervisor's Responsibility:
   - Ensure that the driver has made all the required notifications and has properly filled out all the forms.
   - Investigate the accident and attempt to determine what may have lead to the incident.
   - Discuss your finding of the investigation with the driver and co-workers so that these types of incidents can be avoided in the futures.

g. Vehicle Accident Reporting Procedure
   The EMD employee involved in the accident must:
   - First:
     - Stop immediately and provide needed first aid.
     - Call for an ambulance if necessary

- Avoid obstructing traffic.
- Place emergency flags or flares if available.
- Notify the Police Complaint Board.
- If a death or serious injury has occurred, call the Occupational Safety Office.

- Second:
  - Follow "Accident Reporting Instructions" in the form Gen. 88 packet.
  - Be courteous; avoid arguments.
  - Ask witnesses to sign witness cards.
  - Sign no statements.
  - Admit no negligence or fault.
  - Assume no liability for yourself or the City.
- Third
  - Notify your supervisor that you have been involved in an accident.
  - Completely fill out form Gen. 88. The carbon copies of the form must not contain information on the back portion of the original or City Attorney's copy. The form must be signed, dated, and turned in to the employee's supervisor.
  - If a death or serious injury has occurred, call the City Attorney.
  - Contact Worker's Compensation if a City employee has been injured

Field Sampling

For employees who have been assigned the duty of sample collection, there must be an awareness of the potential hazards involved at both the site and in the sampling subject. The following are general precautions to be observed during sample collection.

a. Use proper equipment for the job. This includes personal protective gear such as eye protection, gloves, boots, or hardhat, when necessary; and equipment required to aid in sampling such as poles and holders for the bottles.
b. No Laboratory Technician should sample alone along the prior to proper training; if possible bring someone along to assist.
c. Be sure samples are secure in the vehicle or mode of transport to avoid the risk of contamination and the possibility of spillage resulting in exposure.
d. Never deliberately touch the water or waste being sampled. Remember that these substances could pose a risk to your health.
e. Disinfect hands and exposed body parts after sampling, and be sure to clean off utensils, gloves, and boots to protect others.

During sampling, safety of the sampler is of prime importance. If a sample location is inaccessible or deemed to be unsafe, no sample is required to be collected and comments

should be noted on the observation sheet. During wet weather, safety consideration may preclude collection of a sample.

Laboratory Safety

The collection and analysis of environmental samples involves contact with samples that may contain agents that pose a microbiological and/or chemical hazard. The primary means of exposure to these microbiological hazards involve body contact during sample collection and hand-mouth or nose contact while handling the samples. Personal protective measures are mandatory while working in the field and laboratory. Following are some key steps to be followed by all laboratory analysts:

a. Assure that appropriate eye protection is worn by all persons, when toxic materials (chemicals or biochemicals) are handled. Contact lenses should not be worn when working with chemicals.
b. Wear appropriate gloves when the potential for contact with toxic materials exists; inspect gloves before each use, wash them before removal, and replace them periodically.
c. Persons doing sampling must wear boots. The boots must be cleaned before entering the building. Boots cannot be worn in the lunchroom, under any circumstances. Steel-toed chemical resistant boots should be worn for the harshest environments, where there is also risk of injury to the foot and toes.
d. Use any other protective and emergency apparel and equipment as appropriate.
e. Remove laboratory coats immediately when exposed to significant contamination.

In addition, persons who work in biological laboratories are often at risk of exposing themselves to a number of infectious agents, especially those known to be indigenous to wastewater. Most persons trained in biological and especially microbiological fields usually are aware of the risks involved, and even if precautions are taken, most of the work-related infections are due to certain practices conducted in the laboratory resulting in the generation of aerosols or through cutaneous pathways. The following guidelines are designed to prevent any exposure of personnel to infectious agents.

1. Hazardous areas and receptacles of contaminated items are to be properly labeled.
2. No eating or drinking in the laboratory. No food or drink is to be stored in laboratory refrigerators, incubators or on bench tops.
3. Store personal effects outside the microbiology laboratory area to prevent contamination. Manager and supervisors are responsible for enforcing this rule.
4. It is policy to wear a lab coat while working in the laboratory. Lab coats and street clothes should be stored separately. Lab coats are prohibited in the lunchroom.

5. Latex or plastic gloves are to be provided and used by employees.
6. Always wash your hands thoroughly after handling sewage, sludge, or receiving water samples of any source before handling food or leaving the lab. "All" samples should be treated as potentially hazardous. Germicidal soap is to be available to all employees, and should be kept in stock.
7. Laboratory workers should not touch their hands to their face, especially the eyes, nose, and mouth when working with wastewater samples.
8. For workers who handle wastewater and its byproducts, it is recommended that they have been vaccinated for polio and tetanus. Persons in poor health and at risk of infection should inform their supervisor, and arrange for an improvement in their personal protection.
9. Never pipette by mouth. Use bulbs or other mechanical means to draw up the liquid.
10. Safety cabinets of the appropriate type and class are to be supplied, maintained, and used.
11. Employees should use the provided bottle carriers when moving reagents, acids, and solvents through the building.
12. Laboratory personnel must follow labeling protocols in the laboratory to prevent mix-ups of reagents, and when possible use the pre-labeled or permanently labeled bottles. Secondary containers are to be labeled as well.
13. In the event of a spill, all possible contaminated surfaces and tools are to be disinfected and the absorbent material placed in a biohazard bag for disposal.